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HAIR ANALYSIS USING PIXE

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内容摘要：

原子荧光和原子反散射分析单根头发中痕量元素的含量及其沿着头发或是在头发的某个横断面上的分佈情况。



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Abstract A simple and new technique for examining single hair strands to obtain linear mass densities, longitudinal profiles and transverse distributions of each trace element is described. It is primarily based upon the PIXE technique, in combination with proton back-scattering. The three main components of this technique are: 1) An accurate way of using an interpolation method to evaluate the magnitude of the correction factor accounting for the proton energy loss and X-ray absorption in the bulk of the hair is formulated; 2) A simple method to qualitatively determine the transverse distribution of each trace element in a hair is introduced and proved to be effective; 3) Proton back-scattering is proved to be capable of providing an ideal linear measure of the geometric hair diameter, one of the most important parameters in quantifying the results of PIXE measurements in mass concentrations. Using the technique, a PIXE system designed and constructed for routine longitudinal scanning of single hair strands is also described.			
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Date October 28, 1983

Li Hong-kou

To the memory of my father

HAIR ANALYSIS USING PIXE

by

LI HONG-KOU

Summary

Acknowledgements

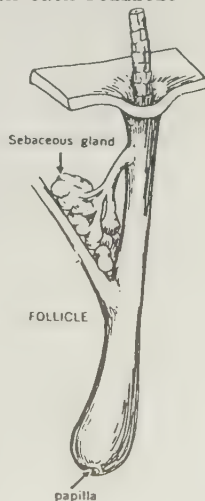
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SUMMARY

1. Introduction

Because trace elements play very important roles in human metabolism and nutrition, it is of great concern to find some simple method of examining an individual's trace element status. Analysis of faeces and urine is often of limited value as they carry information which only reflects the intake on a short term basis, and blood has restricted use because the haemostatic mechanisms operate to suppress variations of concentrations of many trace elements. Elemental concentrations along a single hair strand often constitute a chronologic recording of important aspects of the trace elemental status of the body over a long period of time. Furthermore, hair is a kind of biopsy material which can be easily obtained and transported.

A human scalp hair arises in a tubular hair follicle in the epidermis, which extends down into the dermis, where it is surrounded by connective tissue. The active follicle has an expansion with a concavity in its bottom occupied by a connective tissue papilla. The cells of the papilla form the hair root which develops into the hair shaft. The free end of the shaft protrudes beyond the structure of the skin. One or more sebaceous glands are associated with each follicle. They discharge their secretory product into the upper portion of the follicular canal. When the hair is in a phase of growth (anagen phase), the cells around the papilla differentiate into several types. In certain types of coarse hairs the central matrix cells on top of the convexity of the papilla develop into the medulla of the hair shaft. The next concentric layer of matrix cells keratinizes and develops into the cortex of the hair, the main constituent of the shaft. Its cells carry most of the pigment of the hair. Peripheral to the matrix cells of the cortex lie those of the cuticle of the hair. These cells are the most heavily keratinized and act as a protective layer for the hair. These three layers of cellular components all undergo keratinization in the

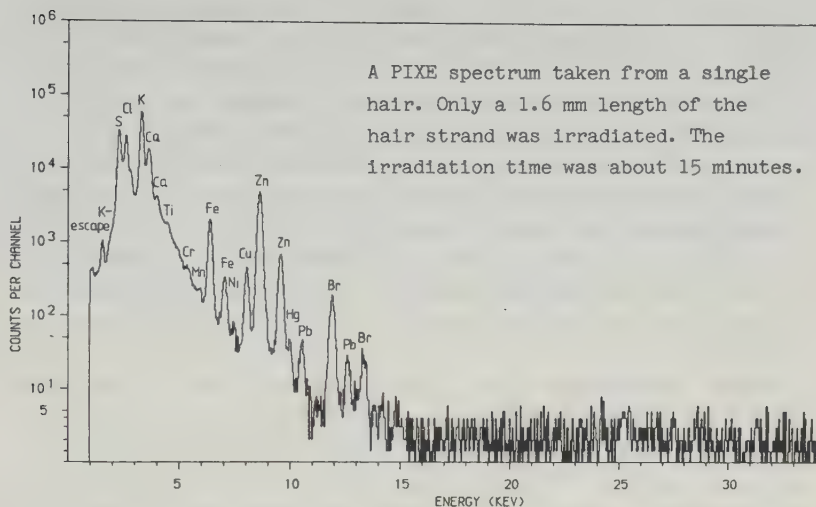


so-called keratogenous zone of the follicle, immediately above the dome of the dermal papilla, and form the solid hair shaft. When using hair as a monitor of trace elements in the body, it is assumed that the trace elements are incorporated into the hair during the formation of the various cellular components in proportion to their levels in other parts of the body, e.g. body fluids and tissues.

Different methods for trace elemental analysis have been applied to single hair strands. Techniques such as neutron activation analysis, atomic absorption spectroscopy and X-ray fluorescence analysis have been used extensively. However, the results have not been very encouraging. The problems are two fold: first, the absolute amount of a trace element in a hair strand is small, which means not only that the method used for hair analysis should be very sensitive, but also that contamination during sample preparation can present very serious problems; second, the concentration of a trace element in a hair strand is a function of many factors, and it is not clear to what extent the measured trace element level reflects internal conditions (nutrition, disease and genetic effect etc.), and to what extent it reflects environmental effects (air, water and soil etc.). Therefore, it is necessary to find a method which can not only accurately quantify the small amounts of trace elements in a hair strand, but also, to a certain extent, assay its endogenous or exogenous origin.

2. The PIXE method

The very promising features of combining X-ray excitation by protons with X-ray detection using a Si(Li) detector for elemental analysis were first described and experimentally demonstrated by Johansson, Akselsson and Johansson in 1970. The work was promptly taken up by many nuclear physicists in other accelerator laboratories, and a rapid development of the technique has followed. Three international conferences on particle induced X-ray emission (PIXE) and its analytical applications have been organized. It is now quite clear that the introduction of PIXE as an analytical tool has created many new possibilities in various different research disciplines (medicine, biology, aerosol science and environmental technology, forensic science, archaeology etc.), of which the work described in this thesis is intended to be an example.



The principle of PIXE analysis may be simply explained as follows: a beam of charged particles (protons, α -particles or other ions) with an energy in the region of 1-5 MeV/u from an accelerator (electrostatic accelerator, cyclotron or an ion accelerator of other type) is used to irradiate a sample, in order to create vacancies in the inner electronic shells of the atoms present in the sample. When the vacancies are filled by electrons from outer shells, X-rays with energies characteristic of each element in the sample will be emitted with certain probabilities. The number of atoms of each element present in the sample can thus be determined by measuring both the energies and intensities of the characteristic X-rays emitted using a solid state detector.

PIXE is a non-destructive, multi-elemental method for fast microanalysis. Ten to thirty elements, heavier than aluminium, can be quantitatively determined in a normal single irradiation. Furthermore, the detection of nuclear reaction products (elastically scattered charged particles, γ -rays etc) can be carried out simultaneously with

PIXE analysis. This extends the analytical capability to many lighter elements (Al, Na, F, C, Be etc.). The mass detection limit for a small sample is low, typically between 0.1 and 10 ng. The speed of performing a PIXE analysis is high. A complete multi-elemental analysis of a specimen can be carried out within minutes.

Papers discussing the application of PIXE to hair analysis began to appear in the literature in the early 1970's. Three different approaches have been used in PIXE analysis of hair samples. The first approach is to use physical or chemical methods to break down the structure of the hair, then form the material into a homogenized thin specimen, and then analyse it using the PIXE method. This approach has two disadvantages. First, all the information relating to the elemental distribution along a hair strand and over its transverse cross section is lost. Second, the contamination in the preparation of the sample often presents serious problems. The second approach is to expose a hair directly to a normal millimetre proton beam for either the analysis of a single piece of hair or a longitudinal scan of the whole hair. The main problem with such an approach is that a hair fibre is a complicated biopsy material, and it is not simple to derive the mass concentrations of the trace elements in the hair from the measured PIXE data. The third approach is to use a proton microprobe to make a PIXE scan across the diameter of a hair. This approach has been used in several laboratories to investigate how various trace elements have been introduced into the hair. However, it takes hours to make such a scan, and the preparation of a hair cross section specimen is also a very tedious task. Hence, it is not very practical to use a proton microprobe to examine single hair strands on a routine basis. This thesis focuses on the second approach offering a procedure for quantification of trace elemental concentrations in single hair strands, that is useful for routine investigations.

3. Thesis

A simple and new technique for examining single hair strands to obtain linear mass densities, longitudinal profiles and transverse distributions of each trace element is described in this thesis. It is primarily based upon the PIXE technique, in combination with proton back-scattering. The three main components of this technique are: 1) An accurate way of using an interpolation method to evaluate the

magnitude of the correction factor accounting for the proton energy loss and X-ray absorption in the bulk of the hair is formulated; 2) A simple method to qualitatively determine the transverse distribution of each trace element in a hair is introduced and proved to be very successful; 3) Proton back-scattering is proved to be capable of providing an ideal linear measure of the geometric hair diameter, one of the most important parameters in quantifying the results of PIXE measurements in mass concentrations. This technique satisfies the demands raised in the introduction: it can not only determine the small amount of a trace element in a hair, but also to a certain extent assay the endogenous or exogenous origin of the element.

Paper I

In this paper the accuracy of the PIXE method applied to a single hair strand is discussed in detail. The discussion is supported both by demonstrating the details in calculating F , the correction factor, in cases where the trace element is uniformly distributed in the bulk of the hair, and by showing the results of PIXE analysis of single hair strands for sulphur and zinc. The geometric diameter of a hair strand is shown to be a more suitable parameter than the linear density in the quantification procedure. It is concluded that the accuracy of the PIXE method does not become considerably lower when it is applied to a single hair strand. Thus accuracy and precision below 10% can be achieved.

Paper II

In this paper it is shown both theoretically and experimentally that the distribution of a trace element over the transverse cross section of a hair can be qualitatively determined by performing PIXE measurements at two different proton energies. A parameter is introduced to qualitatively describe the distribution of a trace element over the transverse cross section of a hair. The parameter is also used in an evaluation of the correction factor by linear interpolation.

Paper III

In this paper it is shown both theoretically and experimentally that the intensity of the back-scattered protons from a surface layer of a hair, which corresponds to the number of counts between two chosen channels in the observed proton back-scattering spectrum, is linearly proportional to the diameter of the hair, and thus provides a convenient tool for determining the most important parameter in quantification of the results of PIXE analysis of single hair strands.

Paper IV

In this paper the PIXE system designed and constructed for routine longitudinal scanning of single hair strands is described. It is a realization of the concepts developed in the above three papers. The technical measures to reduce the heating damage, to obtain a homogeneous beam profile while maintaining the necessary beam intensity, and to correctly integrate the electric charge etc. are also described.

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A QUANTITATIVE BASIS FOR HAIR ANALYSIS USING PIXE

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The PIXE technique offers the possibility of scanning a single hair strand longitudinally with a millimetre proton beam for trace elements. However, the accuracy of the method has been questioned since the quantification of the mass concentration has been a serious problem. In this paper a specific beam-hair-detector geometry is assumed, and the correction factor accounting for the proton energy loss and the X-ray absorption in the hair is calculated. 43 hair segments from 8 individuals, ranging from 45 to 110 μm in diameter were analyzed giving a mean value of 4.32% (standard deviation 0.25%) for sulphur, and a mean value of 149 ppm (standard deviation 35 ppm) for zinc. It is shown that the geometrical diameter of a hair strand is a more suitable parameter than the linear density in the quantification procedure, and that the corrections for the effects of proton energy loss and X-ray absorption in hair are important not only for the determination of the absolute elemental concentrations but also for the determination of their relative longitudinal distributions. The uncertainty in converting the characteristic X-ray intensities to absolute elemental concentrations due to the complexities of the properties of human hair is evaluated. Possible ways of reducing this uncertainty are also discussed. It is concluded that the accuracy of the PIXE method does not become considerably lower when it is applied to single hair strands. Accuracy and precision below 10% may be reached by implementing the procedure and technical measures described.

*On leave from Department of Nuclear Physics, Fudan University, Shanghai, China.

1. Introduction

Hair analysis for trace element concentrations has attracted increasing interest amongst researchers in topics such as toxicology, forensic medicine, nutrition, and environment technology due to the possibility of using the measured trace element levels as a quantitative indicator for trace element levels in other parts of the body, and for the possible interaction of the individual with environmental sources (refs 1-4). The Particle Induced X-ray Emission (PIXE) method, being a technique for fast, reliable multi-elemental analysis at the ppm level in small samples (ref.5), offers the possibility to longitudinally scan a single hair strand for trace element distributions (ref.6), thereby giving a time record of an individual's trace element status. It is relatively easy to expose a single hair strand to a millimetre proton beam, which is readily available from an electrostatic accelerator, and record the X-ray spectrum using a Si(Li) detector. However, difficulties have been met in converting the characteristic X-ray intensities to the absolute elemental concentrations, and the accuracy of the method has been seriously questioned in view of the complexities of the properties of human hair (ref.7). Montenegro et al. (ref.8) proposed a correction factor to account for the effects of the proton energy loss and the X-ray absorption in hair by introducing simplifying approximations, and showed the importance of this correction. However, the approximations introduced in their calculation seem rather crude for lighter elements. The sulphur K X-ray production cross section at a penetration depth of 20-50 μm in hair, for example, may differ from that of the approximation by about 20-60% for 2.5 MeV incident protons. Furthermore, they did not answer the question of how accurate the method was if complexities such as the variable major element composition, the inhomogeneous trace element distribution over the cross section of the hair, the elliptical shape of the cross section, and the possible difference in mass density etc. were taken into consideration. Campbell et al. (ref.9) reported a method in which the longitudinal PIXE scanning of an individual hair with a normal millimetre proton beam provided a position dependence of the trace element concentrations in relative terms, and the subsequent conversion of the hair to a thin specimen for PIXE analysis provided absolute trace element concentrations for the entire hair. It will be

shown in this paper that this method is only suitable for hair with a reasonably constant diameter.

In this paper a specific beam-hair-detector geometry is assumed, and the correction factor for hair which satisfies certain conditions is calculated. The quantification method is experimentally demonstrated, the uncertainties in the quantification procedure due to the complexities of the properties of human hair are evaluated, and possible approaches to reduce them are also discussed.

2. Calculation

The beam-hair-detector geometry is schematically shown in fig.1(a).

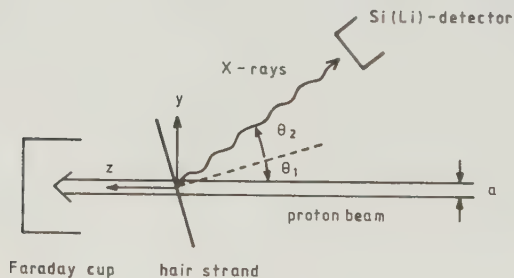


Figure 1(a) The beam-hair-detector geometry (horizontal plane). The Y-axis and the Z-axis of the space coordinate frame are also shown. The X-axis is perpendicular out of the plane of the paper. The dashed line is the normal to the hair strand.

The proton beam has a rectangular shape, and a homogeneous intensity profile in the vertical direction. The counts N_x in a characteristic X-ray peak of a certain element may be expressed as follows

$$N_x = Q/(a \cdot b) \cdot \bar{C} \cdot M \cdot P \cdot F \quad (1)$$

where Q is the total charge of the protons collected in the Faraday cup (μC), a and b are the dimensions of the beam in the horizontal and vertical directions respectively (cm), $\bar{C}$ is the average concentration of the element (g/g), M is the mass (mg) of the bombarded part of the hair strand, P is the sensitivity factor for thin specimen analysis ($\text{counts} \cdot \text{cm}^2 / (\mu C \cdot \text{mg})$), and F is a correction factor accounting for the proton energy loss and the X-ray absorption in the hair matrix. The mass M is equal to $(a \cdot W) / \cos \theta_1$ (see fig.1(a)), where θ_1 is the angle defined by the proton beam and the normal to the hair strand, and W is the linear density of the hair (mg/cm). The correction factor F is defined by the equation

$$F = \frac{1}{M} \int_M \sigma_x(E) / \sigma_x(E_0) \cdot T \cdot C / \bar{C} \cdot dm \quad (2)$$

where σ_x is the X-ray production cross section (which is a function of the proton energy E), E_0 is the incident proton energy, T is the X-ray transmission in the bulk of the hair, and C is the concentration of the element, which is a function of the spatial coordinates in the hair.

The hair, for which the correction factor will be calculated in this section, is assumed to be regular, i.e. satisfy the conditions (a), (b), (c) and (d) in Table 1.

With condition (a) assumed, the proton stopping powers and the X-ray absorption coefficients of the hair may be evaluated. Proton stopping powers and X-ray absorption coefficients of different elements may be found in the literature (refs 11-12). A convenient empirical formula for the calculation of the proton stopping power in hair is suggested as follows

$$S = 0.25 E^{-0.70} \quad (3)$$

where S is the proton stopping power, expressed in $\text{MeV} \cdot \text{cm}^2 / \text{mg}$, and E is the proton energy in MeV. The above formula fits the literature

Table 1

Conditions for a regular hair.

-
- (a) Its major element composition (g/g) is the same as in the hair of Reference Man (ref.10): hydrogen 7.53%, carbon 46.1%, nitrogen 13.7%, oxygen 28.2%, sulphur 4.14%, and calcium 0.30%.
- (b) The elements of interest are uniformly distributed over the cross section of the hair.
- (c) The cross section of the hair is circular.
- (d) The mass density over the cross section is homogeneous, and its value is the same as that of Reference Man, i.e. $\rho_0 = 1310 \text{ mg/cm}^3$ (ref.10).
-

data (refs 10-11) to within about 2% for 0.4-4 MeV protons.

Accordingly, the proton penetration depth l_m (mg/cm^2) in hair can be expressed as a function of the proton energy E and vice versa

$$l_m = \int_{E_0}^E 1/(-S) \cdot dE = 2.35 (E_0^{1.70} - E^{1.70}) \quad (4)$$

$$E = (E_0^{1.70} - 0.425 l_m)^{0.588} \quad (5)$$

An expression for the correction factors can be derived using the definition in eq.(2), substituting the term $\sigma_x(E)/\sigma_x(E_0)$ by the ratio of the ionization cross sections $\sigma(E)/\sigma(E_0)$, which may be calculated by using the empirical formula of ref.13,

$$\sigma(E) = 10^{-24} / U \cdot \exp \left(\sum_{K=0}^5 b_K (\ln(10^3 \cdot E/U))^K \right) \quad (6)$$

where U is the ionization energy in eV, E is the proton energy in MeV, and b_K is a set of constants. The unit of the ionization cross section is 10^{-24} cm^2 . The length of the path (mg/cm^2) in hair for the characteristic X-rays recorded by the Si(Li) detector, as shown in fig.1(b), is $(\rho_0 \cdot l \cdot \cos \theta_1 / \cos \theta_2) = (l_m \cdot \cos \theta_1 / \cos \theta_2)$ if the



Figure 1(b) Path of the detected X-rays.

hair experiences no significant change in its thickness over a length of about 0.1 mm. In this case the X-ray transmission in hair is equal to

$$T = \exp(-\mu \cdot l_m \cdot \cos \theta_1 / \cos \theta_2) \quad (7)$$

where $\mu = \sum_i \mu_i P_i$ is the X-ray mass absorption coefficient of the hair matrix (cm^2/mg), i denotes the major elements H, C, N, O and S etc., in the hair matrix, μ_i is the X-ray mass absorption coefficient of element i (cm^2/mg), and P_i is the elemental concentration (g/g). With condition (b) assumed (see Table 1), the term $C/\bar{C}$ is equal to one. In the coordinate frame O-XYZ, the Z-axis is defined to be parallel to the proton beam axis and the X-axis to be perpendicular to both the proton beam and the hair strand (see fig.1(a), the X-axis is perpendicularly out of the plane of the paper). The differential mass element, dm , in the integration of eq.(2) may be chosen as follows (see fig.1(c))

$$dm = a \cdot g \cdot dl_m \quad (8)$$

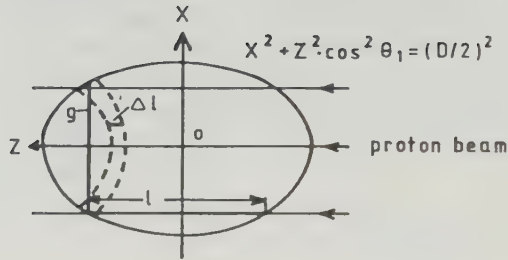


Figure 1(c) The differential mass element:

$$\begin{aligned} dm &= \rho_0 \cdot dV = \rho_0 \cdot a \cdot g \cdot dl = a \cdot g \cdot dl_m \\ &= a \cdot D \cdot (1.0 - (l_m \cdot \cos \theta_1)^2 / (D \cdot \rho_0)^2)^{0.5} \cdot dl_m \end{aligned}$$

where g is a geometric factor (cm). With conditions (c) and (d) assumed, the expression for the geometric factor g can be derived by replacing the coordinates with ($x = 0.5 g$, $z = 0.5 l$) in the equation for an ellipse $x^2 + (z \cdot \cos \theta_1)^2 = (D/2)^2$, and further replacing l with l_m / ρ_0 . The result is as follows

$$\begin{aligned} g_r &= D \cdot (1.0 - (l \cdot \cos \theta_1 / D)^2)^{0.5} = \\ &= D \cdot (1.0 - (l_m \cdot \cos \theta_1)^2 / (D \cdot \rho_0)^2)^{0.5} \end{aligned} \quad (9)$$

where the subscript r denotes that the hair is regular, D is the diameter of the hair in unit length, and l and l_m are the penetration depths in units of length and mass per unit area respectively. The mass M_r of the bombarded part of a regular hair is equal to

$$M_r = 3.14 (0.5 D)^2 \cdot a \cdot \rho_0 / \cos \theta_1 \quad (10)$$

With eqs (7)-(10) the correction factor defined in eq.(2) may be written in the form

$$F_C = 4 \cos \theta_1 / (3.14 \rho_a \cdot D) \cdot \int_0^{\rho_a \cdot D / \cos \theta_1} \bar{G}(E) / \bar{G}(E_0) \cdot T \cdot (1.0 - (1_m \cdot \cos \theta_1)^2 / (\rho_0 D)^2)^{0.5} \cdot d1_m \quad (11)$$

By replacing E and $\bar{G}$ in eq.(11) with eqs (5) and (6) respectively, the values for the correction factors may be acquired through numerical integration.

Some of the results of the calculation are plotted in figs 2(a)-(c). The correction factors are presented as a function of the K_α X-ray energy. The reduction in the magnitude of the correction factor for low energy characteristic X-rays is due to X-ray absorption in the hair. The slow reduction in the correction factor with X-ray energy in the high energy region is due to the fact that the characteristic

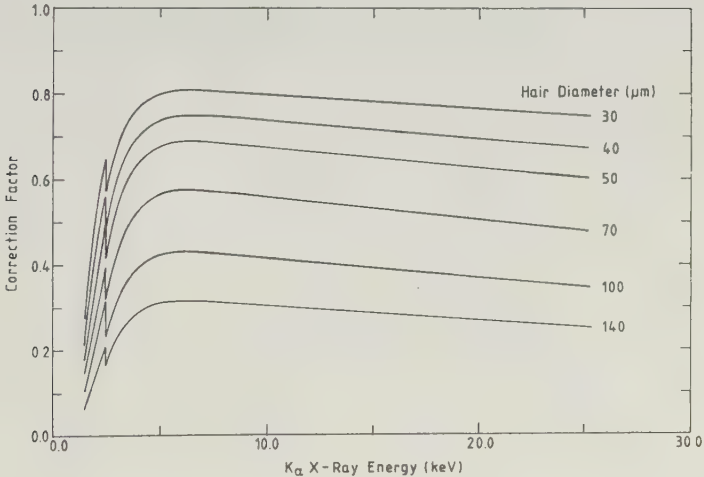


Figure 2(a) The correction factor versus K_α X-ray energy (keV) for varying hair diameter. The hair is assumed to be regular. The incident proton energy is 2.55 MeV. The beam-hair-detector geometry is as shown in fig.1(a), where $\theta_1 = \theta_2 = 22.5^\circ$.

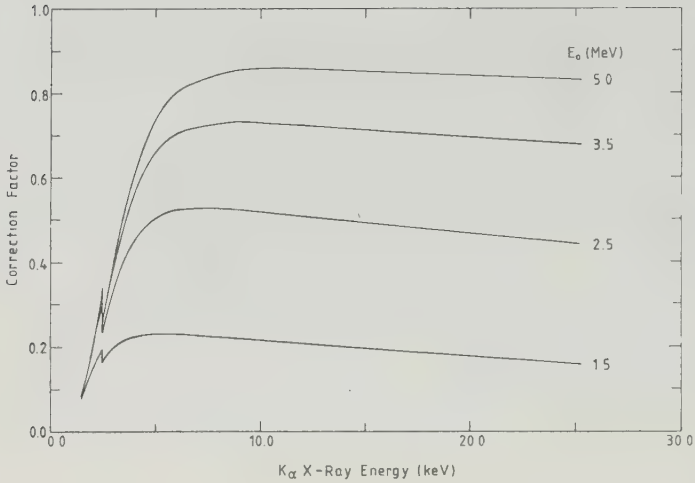


Figure 2(b) The correction factor versus K_{α} X-ray energy (keV) for varying incident proton energy. The hair is assumed to be regular, and its diameter is $80 \mu\text{m}$. The beam-hair-detector geometry is as shown in fig.1(a), but with $\theta_1 = 0$, and $\theta_2 = 45^\circ$.

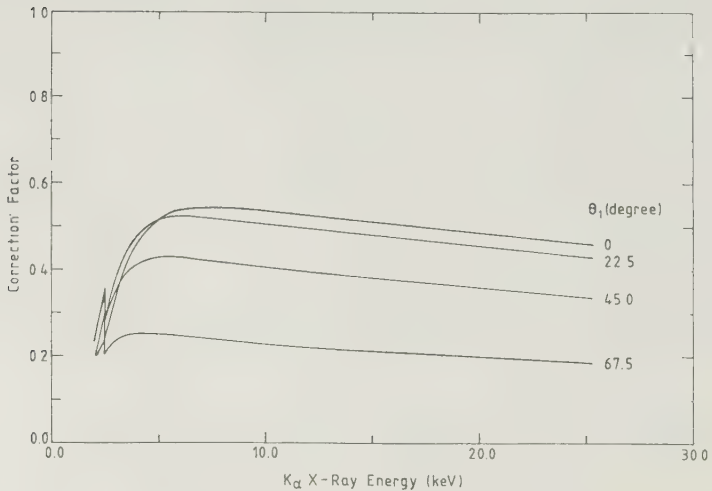


Figure 2(c) The correction factor versus K_{α} X-ray energy (keV) for varying values of θ_1 . The hair is assumed to be regular, and its diameter is $80 \mu\text{m}$. The incident proton energy is 2.55 MeV. The beam-hair-detector geometry is as shown in fig.1(a), where $\theta_1 + \theta_2 = 45^\circ$, i.e. only the angle of positioning of the hair can be changed.

X-ray production cross section of a heavier element is more sensitive to the proton energy than that of a lighter element. The discontinuity at $E = 2.47$ keV is due to the K absorption edge in sulphur. The curves in fig.2(a) correspond to different hair diameters. They show that the correction for the effects of proton energy loss and X-ray absorption in hair are greater for thick hairs than for thin hairs. The curves in fig.2(b) correspond to different incident proton energies. As the incident proton energy E_0 increases, the effect of proton energy loss in hair becomes less important, and the magnitude of the correction factor becomes closer to one. Fig.2(c) shows the variation of the correction factor when the angle of the hair relative to the beam is varied.

3. Experiment

As an example of the application of the quantification method, 43 hair segments from 8 individuals (one Finn, two Chinese, and five Swedes; thereof three females, and five males; all of them healthy, and between the ages of 20 and 40) were collected. The diameters of the hair segments ranged from 45 to 110 μm . The hair segments were ultrasonically cleaned in deionized water for about 10 minutes, and then dried at normal room temperature. Each hair segment, about 2 cm long, was glued at its two ends onto an aluminium frame. No backing material was used. The experimental set-up is shown in fig.3. A detailed description of the irradiation chamber can be found in the literature (ref.14). The beam-hair-detector geometry is as shown in fig.1(a), where $\theta_1 = \theta_2 = 22.5^\circ$. The beam is diffused by a gold foil (1.0 mg/cm^2), and then its central part was selected using a $2.0 \times 4.0 \text{ mm}^2$ collimator. The incident proton energy was 2.55 MeV after the diffusing foil, and the beam intensity after the collimator was controlled so that it did not exceed 10 nA. The integrated charge for each bombardment was $2.0 \mu\text{C}$. The thickness of the hair segments in the vertical direction (along the X-axis, see fig.1(a) and fig.1(c)) was measured with a light microscope both before and after the bombardment. No apparent change was found either in the hair's appearance or in its thickness after the bombardment. Special attention was paid to making sure that each microscopic measurement was made at precisely the same position on the hair segment as the

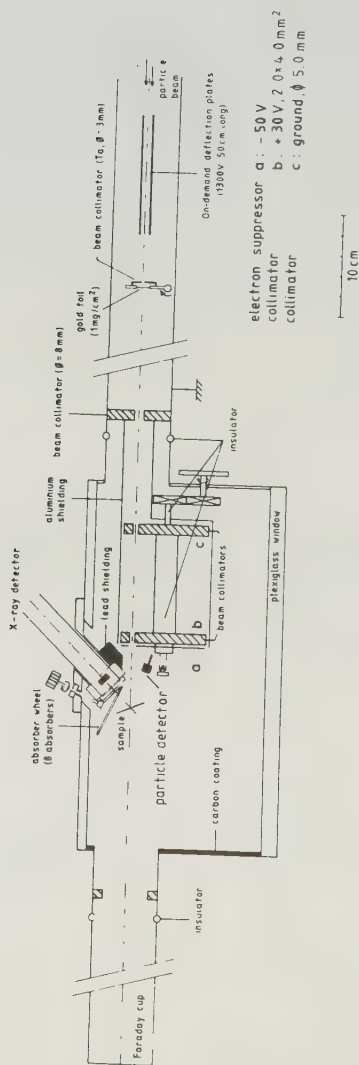


Figure 3

Experimental set-up (horizontal plane).
The beam-hair-detector geometry is as shown in fig.1(a), where $\theta_1 = \theta_2 = 22.5^\circ$. A detailed description of the irradiation chamber can be found in the literature (ref.14).

impingement of the proton beam (ref.15).

The number of counts in the sulphur K X-ray peak, and the zinc K_{α} X-ray peak are plotted in fig.4(a) versus the measured thickness of the hair segment. The data were then converted to mass concentration (g/g) according to eq.(1). The correction factors calculated in Sec.2 were used in the quantification. The final results for zinc and

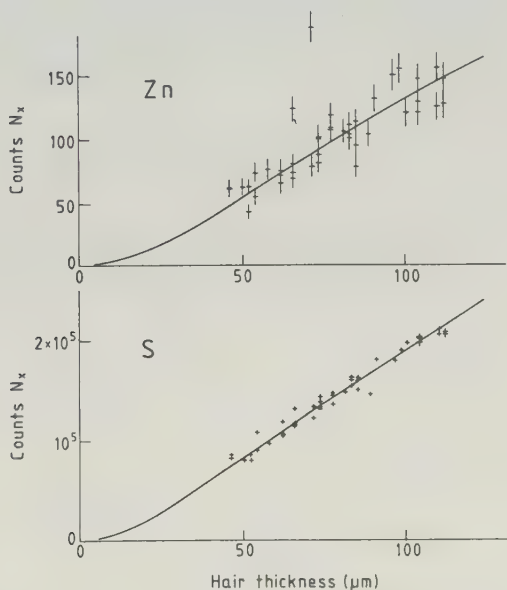


Figure 4(a) Number of counts in the sulphur K X-ray peak, and the zinc K_{α} X-ray peak versus the measured thickness of the hair segments. The solid lines are the least-squares fit to the measured data by eq.(1), where $Q = 2.00 \mu\text{C}$; $a = (2.00 \pm 0.05) \text{ mm}$; $b = (4.00 \pm 0.05) \text{ mm}$; P (sulphur K X-rays) = $= 2.695 \cdot 10^7 \text{ counts} \cdot \text{cm}^2 / (\mu\text{C} \cdot \text{mg})$, and P (zinc K_{α} X-rays) = $= 4.195 \cdot 10^6 \text{ counts} \cdot \text{cm}^2 / (\mu\text{C} \cdot \text{mg})$; the hair segments are assumed to be regular, and the correction factors are calculated (see fig.2(a)); the mass M is evaluated according to eq.(10), and the uncertainty in the microscopic determination of hair diameter D is $\pm 2 \mu\text{m}$. The results of the fits are: the average concentration of sulphur is 4.32% (standard deviation 0.25%), and the average concentration of zinc is 149 ppm (standard deviation 35 ppm).

sulphur concentrations are presented in fig.4(b). The sulphur concentrations of the 43 hair segments are very much the same, and have an average value of 4.32% and a standard deviation of 0.25%. The zinc concentrations of the 43 hair segments scatter about an average value of 149 ppm with a standard deviation of 35 ppm.

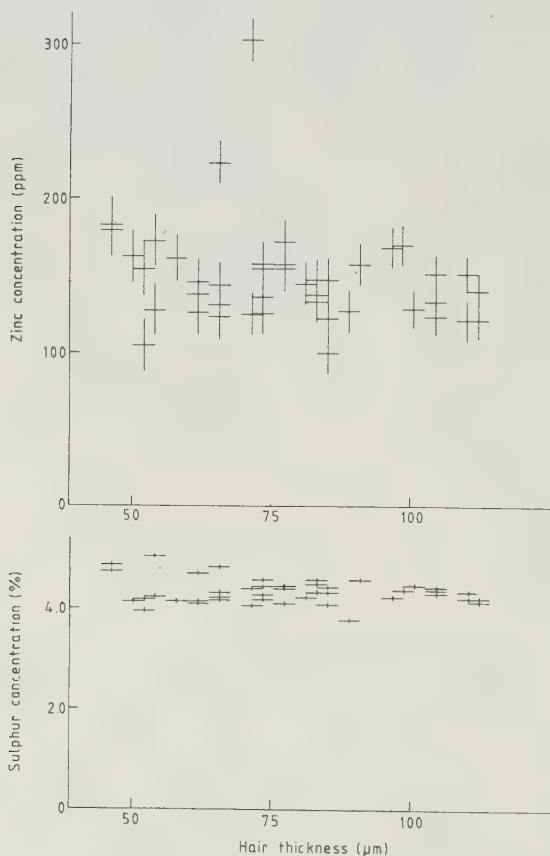


Figure 4(b) The results for sulphur and zinc concentrations versus the measured thickness for 43 hair segments.

Figs 4(a) and (b) show that neither the characteristic X-ray intensity, N_X , nor the result of normalizing it to the linear density of the hair (for a regular hair, the linear density $W = 3.14 (0.5 D)^2 \cdot \rho_0$) can be taken as a relative measure of the elemental concentration due to the difference in thickness of the hair segments. The same is then true for the PIXE scanning of a single hair strand if the diameter of the hair varies considerably along the whole length of the hair. The correction for the effects of proton energy loss and X-ray absorption in hair is important not only for the determination of the absolute elemental concentrations, but also for the determination of their relative longitudinal distribution.

4. Irregularities and possible secondary corrections

According to eq.(1) the average elemental concentration obtained by assuming that the hair under study satisfies the conditions (a),(b),(c) and (d) is

$$\bar{C}_r = N_X \cdot a \cdot b / (Q \cdot P \cdot M_r \cdot F_r) \quad (12)$$

Combining eq.(1) and eq.(12) results in

$$\bar{C} = \bar{C}_r \cdot \eta \quad (13)$$

where

$$\eta = (M_r \cdot F_r) / (M \cdot F) \quad (14)$$

and may be called the secondary correction factor. For a regular hair, the secondary correction factor $\eta_r = 1.0$.

However, a real hair strand is likely not to be regular. The following discussion will assume that only one of the regular conditions (see Table 1) is violated at each time.

1) An inhomogeneous elemental distribution across the diameter of the hair

First, let us consider the case where the hair is assumed to satisfy conditions (a), (c) and (d) but not (b) (see Table 1). The following formula generally holds in this case

$$\eta_s < \eta < \eta_c \quad (15)$$

where η_s is the secondary correction factor in the case where the element of interest is wholly distributed over the surface of the hair, and η_c is the secondary correction factor in the case where the element of interest is totally concentrated at the central axis of the hair. Cylindrical symmetry of the elemental distribution in hair is assumed in writing down formula (15).

η_s and η_c may be evaluated according to their definitions (ref.16). The results of the calculation are presented in fig.5. The

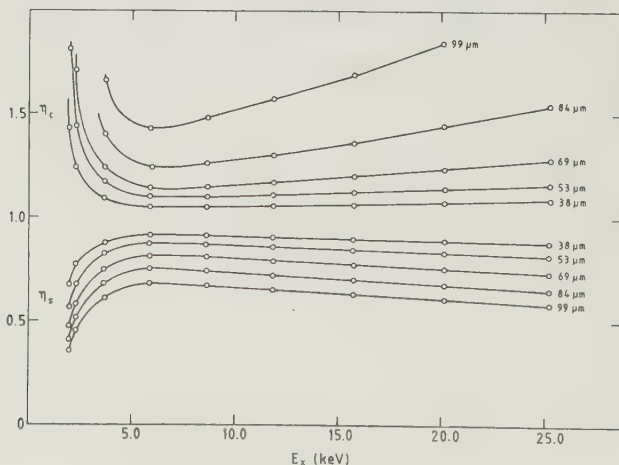


Figure 5

The secondary correction factors η for surface distribution and for central distribution versus the characteristic K X-ray energy E_x (keV). The incident proton energy is 2.55 MeV. The beam-hair-detector geometry is as shown in fig.1(a), where $\theta_1 = \theta_2 = 22.5^\circ$. The curves correspond to different hair diameters.

maximum error due to an unknown elemental distribution for a hair of $70\text{ }\mu\text{m}$ in diameter, for example, is about $\pm 20\%$ for elements with characteristic K_{α} X-ray energy $E_x > 4\text{ keV}$. The values of h_s and h_c both approach 1.0 as the diameter of the hair decreases. Therefore, smaller errors occur for thin hairs than for thick hairs due to the unknown elemental distributions. Another point is that the higher the incident proton energy E_0 used, the smaller the errors which would result from such an unknown elemental distribution. The uncertainty due to an unknown elemental distribution increases rapidly as the characteristic X-ray energy becomes close to 4 keV or less. This is due to X-ray absorption in the hair.

A simple PIXE method using normal millimetre proton beams for determination of the elemental distribution across the diameter of a hair strand is described elsewhere (ref.16). The secondary correction for the effect of an inhomogeneous distribution over the cross section of a hair strand can be made with the help of that method.

2) Irregular shape

The hair under discussion in this section is assumed to satisfy conditions (a), (b) and (d) but not (c) (see Table 1). To make a quantitative estimate it is assumed that the cross section of the hair is elliptic, and one of its axes is parallel to the X-direction (see fig.1(c)). The length of this axis is denoted by the letter D (although the cross section of the hair is not circular). The length of the other axis of the elliptic cross section is equal to $\alpha_1 D$. The equation for the ellipse then takes the form $x^2 + (z \cdot \cos \theta_1 / \alpha_1)^2 = (D/2)^2$. The geometric factor turns out to be $g = D \cdot (1.0 - (1_m \cdot \cos \theta_1)^2 / (\alpha_1 \cdot D \cdot \rho_0)^2)^{0.5}$. The following formula can then be derived using eqs (14), (2), (8) and (9)

$$h_e = F_r(D) / (\alpha_1 F_r(\alpha_1 D)) \quad (16)$$

where $F_r(D)$ and $F_r(\alpha_1 D)$ are the correction factors for the regular hairs of diameter D and diameter $\alpha_1 D$ respectively. The correction factor calculated in Sec.2 can now be used to evaluate the magnitude of the secondary correction factor h_e for elliptical hairs. Fig.6 shows an example: the thickness of the hair in the X-direction is determined to be $70\text{ }\mu\text{m}$, and its thickness in the other direction is

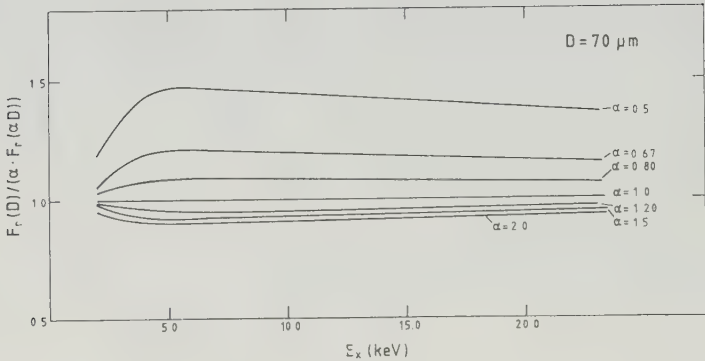


Figure 6

The ratio $F_r(D)/(\alpha \cdot F_r(\alpha D))$ versus the characteristic K_α X-ray energy E_x (keV). The beam-hair-detector geometry is as shown in fig.1(a), where $\theta_1 = \theta_2 = 22.5^\circ$. The incident proton energy is 2.55 MeV. $F_r(D)$ is the correction factor for a regular hair of diameter D , and $F_r(\alpha D)$ is the correction factor for a regular hair of diameter αD . α can be defined either as α_1 , the ratio of the two axes of an elliptic hair (see text), or as α_2 , the ratio of the true mass density of the hair to the mass density of Reference Man's hair. In either case the ratio $F_r(D)/(\alpha F_r(\alpha D))$ is taken as the secondary correction factor.

assumed to be 35 μm , 47 μm , 56 μm , 70 μm (round hair), 84 μm , 105 μm and 140 μm . When a secondary correction is not made, the errors are within 20% for a hair of $D = 70 \mu\text{m}$ if the length of the other axis of the hair is between 55 and 140 μm . The secondary correction for a certain irregular shape is less significant for thick hairs than for thin hairs. In this connection, it should be noted that the lower the incident proton energy E_0 , the smaller the error which results from the irregular shape of the hair. Note that this behaviour is opposite to that obtained from the discussion of an inhomogeneous elemental distribution over the cross section of a hair strand.

It is possible to rotate the hair while it is being analysed. In this case an average value for the hair diameter can be obtained by using the proton back-scattering method (ref.15), and the error due to the unknown shape would thus be considerably reduced.

3) Variable major element composition

In this section the hair under discussion is assumed to satisfy conditions (b), (c) and (d) but not (a) (see Table 1). The change in the values of the X-ray absorption coefficients and the proton stopping powers due to an increase or decrease in the amount of a certain element in the hair may be calculated using the formulae

$$\frac{\Delta \mu}{\Delta p_i} = (\mu_i - \mu) / (1 - p_i) \quad (17)$$

$$\frac{\Delta S}{\Delta p_i} = (S_i - S) / (1 - p_i) \quad (18)$$

where i denotes the major elements in the hair H, C, N, O, S and Ca etc., and Δp_i is the increase in the element i (in unit g/g); μ_i and S_i are the X-ray mass absorption coefficient (cm^2/mg) and the proton stopping power ($\text{MeV} \cdot \text{cm}^2/\text{mg}$) for the element i , and $\Delta \mu$ and ΔS are the changes in the values of the X-ray mass absorption coefficient and the proton stopping power respectively in hair due to the change Δp_i . The relative changes in values of X-ray absorption coefficients and proton stopping powers in human hair, $\Delta \mu / \mu$ and $\Delta S / S$, due to the relative change in the concentration of each major element, $\Delta p_i / p_i$, are evaluated. The results are listed in Table 2. It is clear that the mass absorption coefficients are most sensitive to the relative change in sulphur content and the proton stopping powers are most sensitive to the relative change in hydrogen content. The errors due to the uncertainties in the values of the mass absorption coefficients and the proton stopping powers in quantifying the PIXE results may be obtained by direct calculation. A decrease or increase of 100% in sulphur content in a 70 μm thick hair would result in errors of about $\pm 10\%$ in the calcium content and $\pm 3\%$ in the manganese content, and result in no significant errors for elements lighter than sulphur or heavier than manganese. A decrease or increase of 100% in the hydrogen

Table 2

The relative changes in values of X-ray absorption coefficients and proton stopping powers in human hair due to the relative change in the concentration of each major element.

Element	H	C	N	O	S	Ca
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$$|\gamma_{\mu}| = \left| \frac{\Delta\mu/\mu}{\Delta p_i/p_i} \right| < 0.09 < 0.33 < 0.06 < 0.30 < 0.34 < 0.05$$

$$|\gamma_S| = \left| \frac{\Delta S/S}{\Delta p_i/p_i} \right| < 0.21 < 0.17 < 0.03 < 0.10 < 0.02 < 0.002$$

* $|\gamma_{\mu}|$ is evaluated for 1-30 keV X-rays, and $|\gamma_S|$ is evaluated for 0.4 - 4 MeV protons.

content in a 70 μm thick hair would result in errors of about $\pm 10\%$ for heavy elements ($E_x > 10$ keV), $\pm 7\%$ for intermediate elements ($6 \text{ keV} \leq E_x \leq 10 \text{ keV}$) and $\pm 5\%$ for light elements ($E_x < 6 \text{ keV}$). These data are calculated with $E_0 = 2.55 \text{ MeV}$ and $\theta_1 = \theta_2 = 22.5^\circ$.

- 4) Differing mass density and the possibility of inhomogeneous mass density distribution

Finally, consider the case where the hair is assumed to satisfy conditions (a), (b) and (c) but not (d) (see Table 1). With eqs (14), (2), (8) and (9) the following secondary correction factor $\mathcal{H}_{\bar{p}}$ can be derived

$$\mathcal{H}_{\bar{p}} = F_r(D) / (\alpha_2 \cdot F_r(\alpha_2 D)) \quad (19)$$

where $\alpha_2 = \bar{\rho} / \rho_0$, $\bar{\rho}$ is the average mass density of the hair under discussion. A deviation of $\pm 20\%$ in the mass density of the hair from the value $\rho_0 = 1310 \text{ mg/cm}^3$ would result in an error which is less than $\pm 10\%$ for a hair of $70 \mu\text{m}$ in diameter, as shown in fig.6. The error due to differing mass density can be corrected for as the hair mass density can be determined directly by weighing. The hair mass density over its cross section may not be homogeneous (less dense in the centre, for example), but it has no significant effect because only the integrated mass thickness (mg/cm^2) is sensitive to the processes of proton energy loss and X-ray absorption. The error due to an inhomogeneous mass density distribution over the cross section of the hair is very small and can be neglected.

To summarize, it is concluded that the accuracy of the PIXE method does not become considerably lower when it is applied to single hair strands. Accuracy and precision below 10% may be reached by implementing the procedure and technical measures described in this paper.

Acknowledgements

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A SIMPLE METHOD FOR DETERMINING OF THE ELEMENTAL DISTRIBUTION OVER THE TRANSVERSE CROSS SECTION OF A HAIR

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The increase in the yield of the characteristic X-rays from an element in a hair with the energy of the incident proton beam depends significantly on the distribution of the element over the transverse cross section of the hair. Using this phenomenon a convenient method for a qualitative determination of the elemental distribution over the transverse cross section of a hair is described and experimentally tested.

1. Introduction

The common hypothesis in hair analysis is that the measured trace element levels in hair can be used as a quantitative indicator for the amount of the trace element in other parts of the body, and for the exposure of the person to various environmental sources (refs 1-4). However, it is found that bulk analysis for trace elements in hair is of limited use for this purpose since it is not clear to what extent the measured trace element level reflects the internal bodily conditions (nutrition and health status, genetic disposition etc), and to what extent it is due to the direct interaction of the hair with external sources (air pollutants, shampoo etc) (ref.5). In some cases the trace elements may be introduced in sample preparation and handling, while some endogeneous trace elements may, to a certain

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extent, be removed by improper washing procedures (ref.6-8). It would, therefore, be of great interest to develop a technique which not only allows the determination of the absolute amounts of the trace elements in hair, but also gives information about their distribution over the transverse cross section thus indicating to what extent the elements are exogeneous or endogeneous.

The microbeam PIXE technique offers the possibility of studying the elemental distribution over the transverse cross section of a hair (ref.9). Work has been done with this technique to investigate how trace elements have been introduced into the hair with the intention that this will lead to a better understanding of the data obtained from a bulk analysis (refs 10-12). However, a scan across the diameter of a hair may take hours, and the preparation of a hair cross section specimen is also a tedious procedure. Therefore, it does not seem feasible to use microbeam PIXE analysis as a routine technique to give information on the origin of the trace elements detected in single hair strands.

In this paper a simple method for a qualitative determination of the elemental distribution over the transverse cross section of a hair is described and experimentally tested. The method is reliable and straightforward, and needs no instrumentation other than that of a normal macrobeam PIXE set-up. There is no need to section the hair, and the method is primarily non-destructive. With this method the absolute trace element concentrations as well as their distributions over the transverse cross section of the hair are determined by simply making macrobeam PIXE measurements at two or more different proton energies.

2. Theory

The beam-hair-detector geometry is schematically shown in fig.1. The proton beam has a rectangular shape, and a homogeneous intensity profile in the vertical direction. The number of counts, N_x , in a characteristic X-ray peak of a certain element may be expressed as follows

$$N_x = Q / (b \cdot \cos \theta_1) \cdot \rho_l \cdot P \cdot F \quad (1)$$

where Q is the total charge of the protons collected in the Faraday

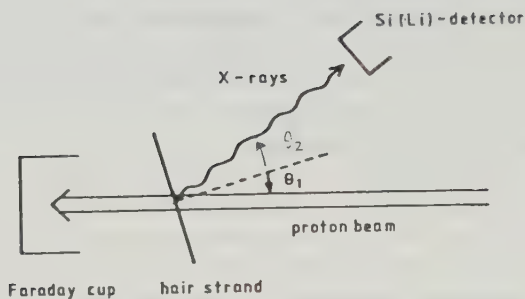


Figure 1 The beam-hair-detector geometry (horizontal plane).

cup (μC), b is the size (cm) of the proton beam in the vertical direction (the hair strand is horizontally positioned), θ_1 is the angle defined by the proton beam and the normal to the hair strand, ρ_L is the linear mass density of the element along the hair ($\mu\text{g}/\text{cm}$), P is the sensitivity factor for thin foils ($\text{counts}\cdot\text{cm}^2/(\mu\text{C}\cdot\mu\text{g})$), and F is the correction factor for proton energy loss and X-ray absorption in the bulk of the hair.

The yield, Y , of the characteristic X-rays per unit charge, as a function of the energy E_1 of the incident proton beam normalized to that at an energy E_0 , is thus equal to

$$Y(E_0, E_1) = \frac{\sigma(E_1)}{\sigma(E_0)} \cdot \frac{F(E_1)}{F(E_0)} \quad (2)$$

where σ is the ionization cross section ($P = \sigma \cdot \text{constant}$), which can be evaluated using the empirical formula of Akselsson and Johansson (ref.13). The value of the correction factor F depends on the distribution of the element over the transverse cross section of the hair. The calculation of the correction factor in the case where the element is uniformly distributed over the transverse cross section of a hair can be found in a previous paper (ref.14), and the calculation of the correction factor in cases where the elements are either completely distributed on the surface or totally concentrated at the centre of the hair are described in an appendix to this paper. Thus, we may calculate the function $Y(E_0, E_1)$ for the three different cases. The following inequalities generally hold

$$Y_s < Y_u < Y_c \quad \text{if } E_1 > E_0 \quad (3)$$

where the subscripts s, u and c denote the cases of surface distribution, uniform bulk distribution and central distribution, respectively. We will assume the condition $E_1 > E_0$ throughout this paper.

In general the measured relative yield Y may be somewhere between Y_s and Y_c . We introduce the following parameter

$$X = \begin{cases} (Y_u - Y) / (Y_u - Y_s) & (Y \leq Y_u) \\ (Y_u - Y) / (Y_c - Y_u) & (Y > Y_u) \end{cases} \quad (4)$$

for a qualitative description of the different elemental distributions over the transverse cross section of the hair. $X = 0$ corresponds to the uniform bulk distribution, $X = 1$ the surface distribution, and $X = -1$ the central distribution.

The correction factor F may be considered to be a function of the measured relative yield Y , and can thus be evaluated using the linear interpolation method

$$F = \begin{cases} F_u + X \cdot (F_s - F_u) & (Y \leq Y_u) \\ F_u + X \cdot (F_u - F_c) & (Y > Y_u) \end{cases} \quad (5)$$

3. Experimental methods

Materials

To test the method and demonstrate its applicability, two hairs were analysed using this technique.

The first hair strand (hair-1) had an extremely high lead content as found in a longitudinal PIXE scan. A thin cross section specimen of this hair was also prepared for a comparative study using a proton microprobe. A short piece of the hair (~ 3 mm) was cut from the hair strand near its tip and placed in carboxymethyl cellulose which had been swelled in distilled water. It was then immediately quench-frozen in liquid nitrogen. A thin section ($< 5 \mu\text{m}$) was obtained by manual

sectioning with a specimen knife of glass at a temperature of -100°C on a Riecher OMU3 FC2 cryoultramicrotome. The hair section was placed between two $2\text{ }\mu\text{m}$ thick plastic foils (Kimfol), and then transferred to circular specimen holders allowing free passage of the protons during irradiation.

The second hair (hair-2) was found to contain very high chlorine content in a previous PIXE analysis. It is the purpose of this examination to see whether it has a surface distribution and thus may be attributed to some exogeneous source.

The transverse distributions of other trace elements in the hairs were also examined.

Macrobeam PIXE measurements

The proton beam was delivered by an electrostatic accelerator (Pelletron 3UDH). The beam-hair-detector geometry is as shown in fig.1, where $\theta_1 = \theta_2 = 22.5^{\circ}$. The beam was diffused by a gold foil (1.0 mg/cm^2), and its central part was selected using a $2.0 \times 4.0\text{ mm}^2$ tantalum collimator with its long side perpendicular to the hair segment. The hair segment was about 2 cm long, and glued by its two ends onto an aluminium frame. No backing material was used. The characteristic X-rays were detected in an 80 mm^2 Si(Li) detector (Kevex, nominal resolution 158 eV at 5.9 keV). A detailed description of the PIXE set-up and the design of the irradiation chamber for PIXE work in Lund can be found in the literature (refs 15-16). The beam current after the collimator was kept below 10 nA to avoid heating damage to the hair during irradiation. The hair diameters were measured at the point of interest with a light microscope both before and after irradiation. It was found that the hair diameter did not change during irradiation. The number of characteristic X-ray counts accumulated should be large enough to avoid uncertainty in the determination of the elemental transverse distribution in the hair due to bad statistics. In this experiment the PIXE measurements were performed at three different proton energies. Proton energies were chosen in the interval 2.0 to 3.5 MeV. The lower limit assures satisfactory counting statistics, and proton energies in the major part of the hair which are sufficiently high to allow accurate estimation of X-ray cross sections from an empirical formula such as the one given in ref 13. The higher limit is within the energy range

well tested for our PIXE set-up. Thus the measured characteristic X-ray yields at the proton energies of 3.00 MeV and 3.40 MeV were normalized to the yield at the proton energy of 2.05 MeV. The values of the parameter X were calculated according to formula (4) for the proton energy E_i equal to 3.00 and 3.40 MeV, respectively. The uncertainties in X values (counting statistics not included) were estimated to about 0.1.

The linear mass densities ($\mu\text{g}/\text{cm}$) of the elements were evaluated using formulae (1) and (5), and subsequently converted to the bulk concentrations (g/g), the average bulk concentrations (g/g) and the surface densities ($\mu\text{g}/\text{cm}^2$) for the cases of uniform bulk distributions, non-uniform bulk distributions and surface distributions, respectively. In case of a surface distribution, the thickness of a thin layer on the surface of the hair can be evaluated by assuming the identity of the chemical compound, in which the element is present.

The uncertainty is composed firstly of the uncertainty from the PIXE method as applied to analysis of hair strands and secondly of the uncertainty due to counting statistics. The first component is estimated to 10%-confer ref.14. Thus 10% is added quadratically to the uncertainties due to counting statistics (one S.D.) in order to obtain a measure of the uncertainties in the linear mass density and concentration values given in this paper.

Microbeam PIXE measurements

An adjustable collimator is situated after the accelerator at a distance of 4 metres from the sample chamber. With the aid of micrometre screws the dimensions of this object collimator can be set independently from 10 to 1500 μm in two perpendicular directions. A proton beam of energy 2.55 MeV was delivered by the accelerator. With 2 quadrupole magnets positioned about 0.3 metres in front of the sample, the experimental demagnification factors were 8 and 38 in the horizontal and vertical planes respectively. The chamber vacuum was about 10^{-5} torr, and the maximum beam intensity obtained was 1-3 $\text{pA}/\mu\text{m}^2$. The sample holder could be moved by remote control in steps of 1 μm or more in both horizontal and vertical directions. To identify and position the samples they were illuminated by an external light source of high intensity through a system of mirrors and windows. Viewing was

carried out using a stereomicroscope. The beam was focused on an area of $8 \times 25 \mu\text{m}^2$, and the specimen was moved perpendicular to the long side of the beam spot in $5 \mu\text{m}$ increments in order to scan the hair across the diameter. The beam current used was about 0.3 nA , and the accumulated charge was $0.1 \mu\text{C}$ per analysed point. The measured characteristic X-ray yields at each point of the scan were normalised to the yield of sulphur, which was taken as a measure of the mass thickness (mg/cm^2) at each point.

4. Results and discussion

Hair-1

The results of the macro PIXE measurements are shown in figs 2(a)-(f).

The measured yields of the lead L_{α} X-rays turned out to be somewhere between the u-curve and the s-curve. The value of the parameter X for lead was found to be 0.60 . Hence, it has a non-uniform bulk distribution, with a higher concentration on the surface than at the centre. The amount of lead calculated is $(0.55 \pm 0.07) \mu\text{g}/\text{cm}$, which corresponds to an average bulk concentration of $(0.92 \pm 0.12) \%$.

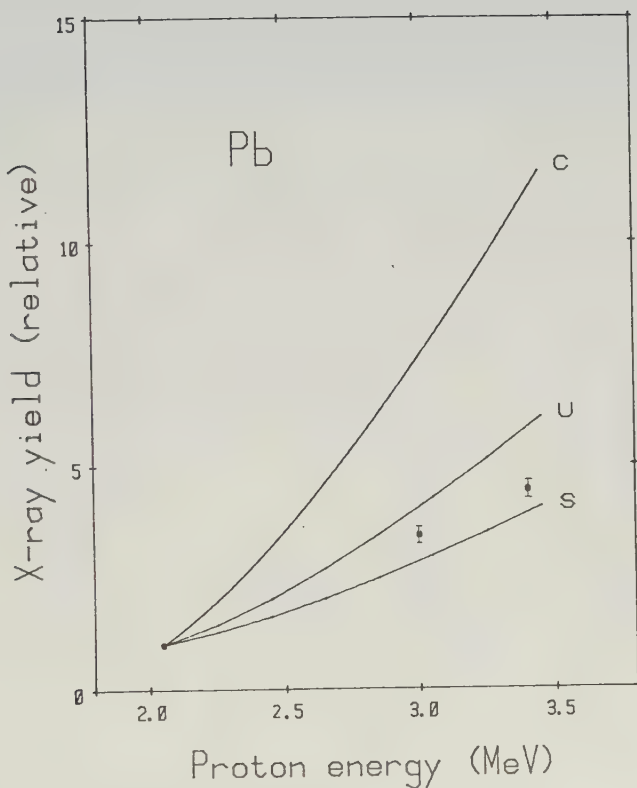


Figure 2(a) Lead L_{α} X-ray yield (relative) plotted versus the proton energy. The hair diameter is $(76 \pm 2) \mu m$. The lines are the calculated s, u, and c curves. And the points are the experimental data. The measured characteristic X-ray yields at the proton energies of 3.00 MeV and 3.40 MeV are normalized to the yield at the proton energy of 2.05 MeV. The indicated errors are statistical (one S.D.).

The measured yields of the sulphur K X-rays are very close to the u-curve. The evaluated X-value for the sulphur distribution is -0.02 . Hence, sulphur has a uniform bulk distribution. This justifies the approach of using the sulphur X-ray yield as a measure of the mass thickness of the thin hair section specimen in the micro PIXE measurements. The concentration of sulphur in this hair was calculated to be $(3.71 \pm 0.37)\%$.

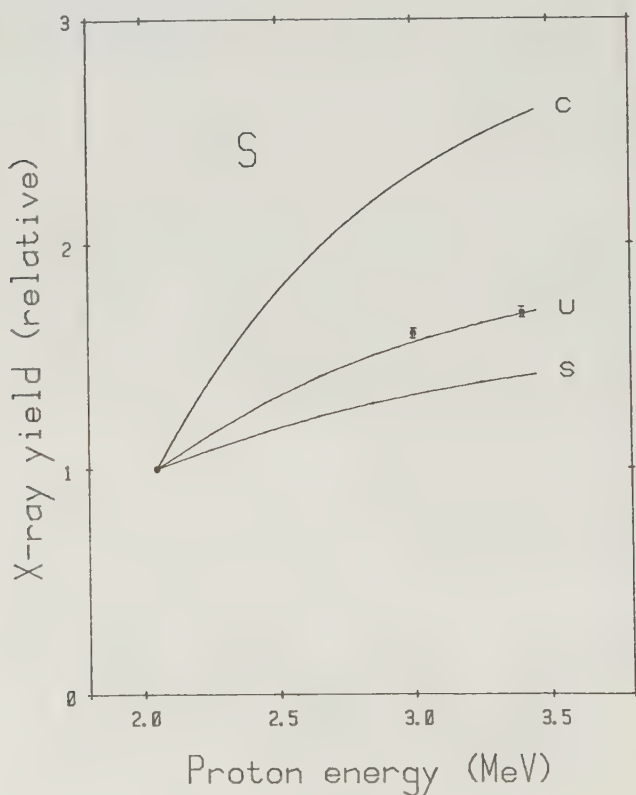


Figure 2(b) Sulphur K X-ray yield (relative) plotted versus the proton energy. For other details see caption to fig.2(a).

The measured yields of the potassium K X-rays are also close to the u-curve. The X-value for the potassium distribution in this hair is 0.15. Hence it is basically a uniform bulk distribution, perhaps with a little higher concentration on the surface than at the centre. The average bulk concentration of potassium was calculated to be $(0.18 \pm 0.02)\%$.

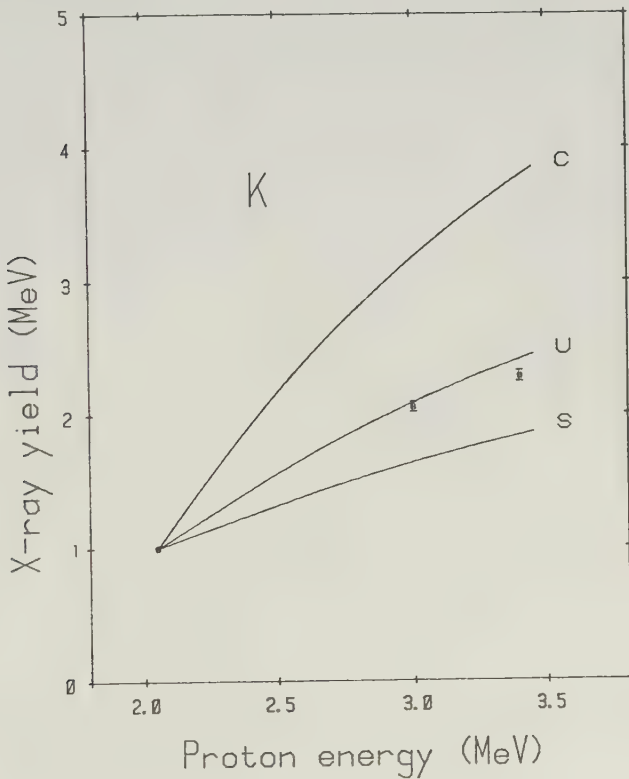


Figure 2(c) Potassium K X-ray yield (relative) plotted versus the proton energy. For other details see caption to fig.2(a).

The X-value for the calcium distribution in this hair is 0.60. Hence, calcium has a similar distribution to that of lead in this hair. The amount of calcium was calculated to be $(0.55 \pm 0.06) \mu\text{g}/\text{cm}$, which corresponds to an average bulk concentration of $(480 \pm 50) \text{ ppm}$.

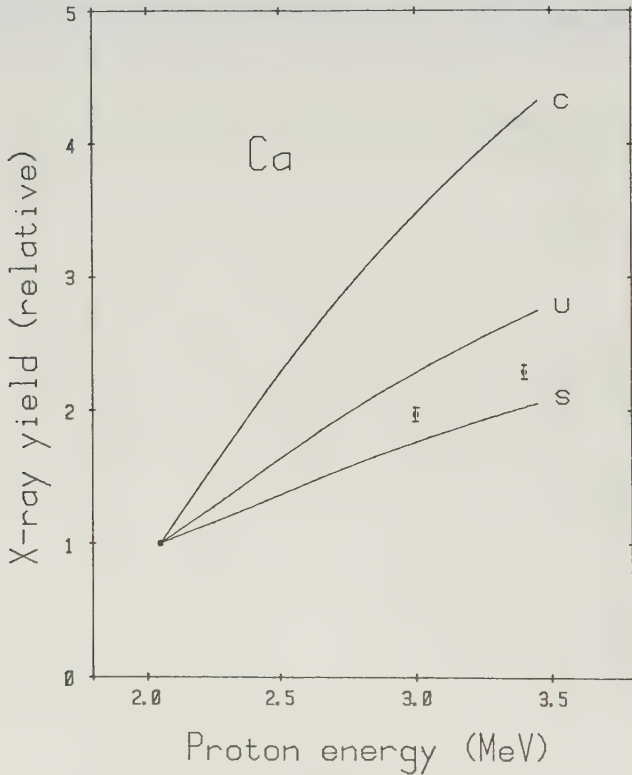


Figure 2(d) Calcium K X-ray yield (relative) plotted versus the proton energy. For other details see caption to fig.2(a).

The X-value for the iron distribution was found to be 0.50. Therefore, it also has a similar distribution to that of lead in this hair. The calculated average bulk concentration of iron is (180 ± 25) ppm.

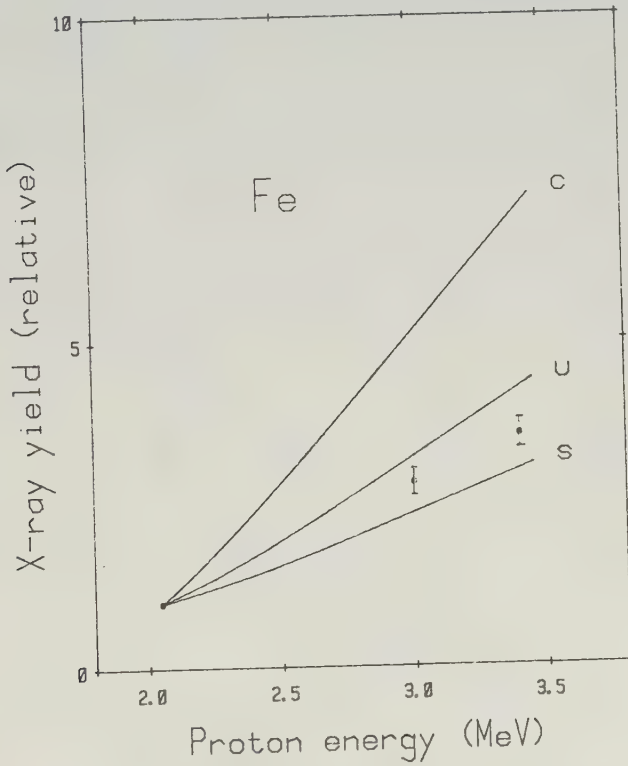


Figure 2(e) Iron K X-ray yield (relative) plotted versus the proton energy. For other details see caption to fig.2(a).

The measured yields of zinc are very close to the u-curve. The X-value for the zinc distribution in this hair is 0.10. Hence, it has a similar distribution to that of potassium in this hair. The calculated average bulk concentration of zinc is (150 ± 23) ppm.

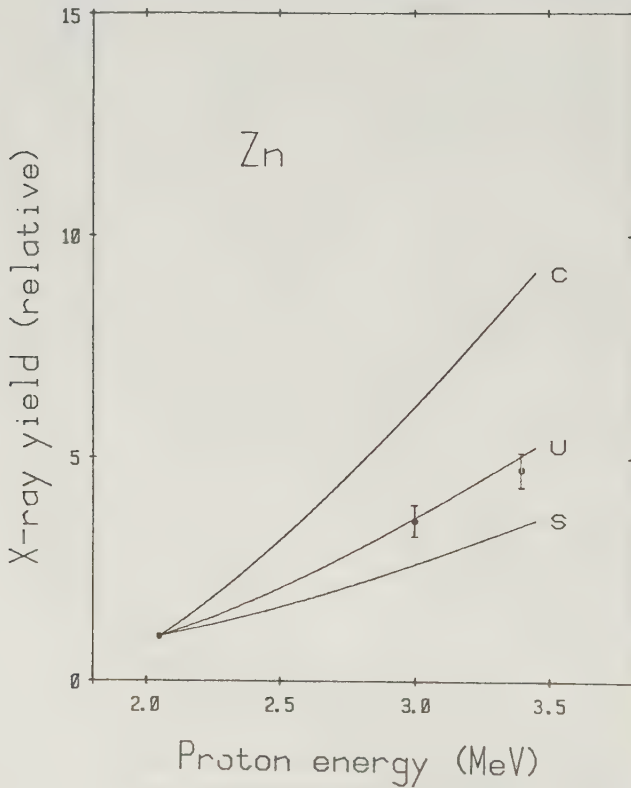


Figure 2(f) Zinc K X-ray yield (relative) plotted versus the proton energy. For other details see caption to fig.2(a).

The results of the micro PIXE scan across the diameter of hair-1 are shown in figs 3(a)-(e). The extent of the hair section analysed is given by the broken lines (cuticle). For potassium and zinc the distributions are approximately uniform, which is in good agreement with the results of the macro PIXE measurements. For calcium, iron and lead the radial scans clearly show a higher concentration near the surface, which is also in good agreement with the results from the macro PIXE measurements.

Since the hair section is taken close to (< 2 cm) where the macro PIXE radial profile measurements were made, the results of the micro PIXE measurements clearly support the macro PIXE technique described.

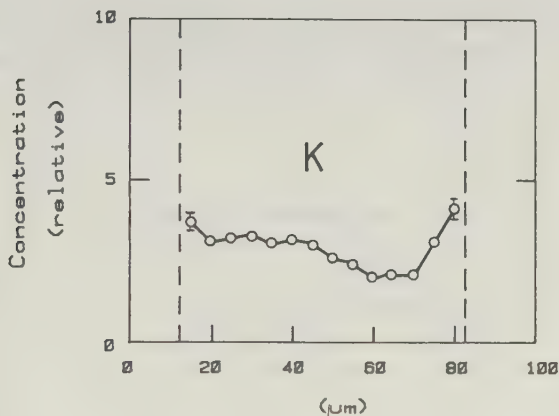


Figure 3(a) Results of the microbeam PIXE scan of hair-1 for potassium. The beam was focused on an area of $8 \times 25 \mu\text{m}^2$, and the specimen was moved in $5 \mu\text{m}$ increments in order to scan the hair across the diameter. The beam current used was about 0.3 nA, and the accumulated charge was 0.1 μC per analysed point. The measured characteristic X-ray yields at each point of the scan are normalised to the yield of sulphur, which is taken as a measure of the mass thickness (mg/cm^2) at each point. The indicated errors are statistical (one S.D.).

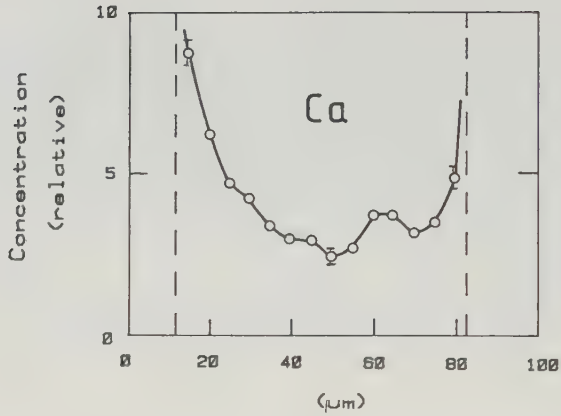


Figure 3(b) Results of the microbeam PIXE scan of hair-1 for calcium. For other details see caption to fig.3(a).

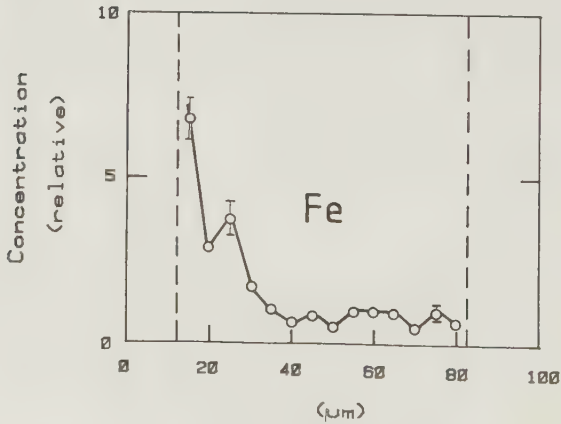


Figure 3(c) Results of the microbeam PIXE scan of hair-1 for iron. For other details see caption to fig.3(a).

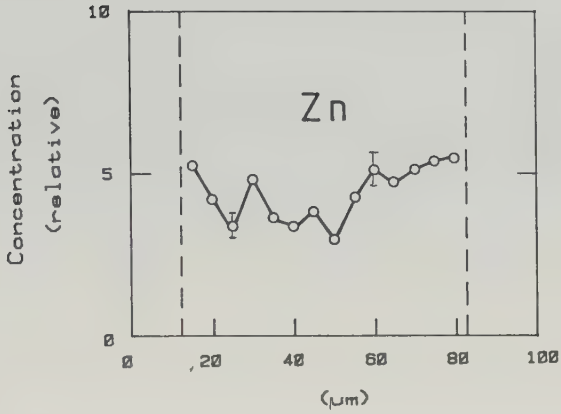


Figure 3(d) Results of the microbeam PIXE scan of hair-1 for zinc. For other details see caption to fig.3(a).

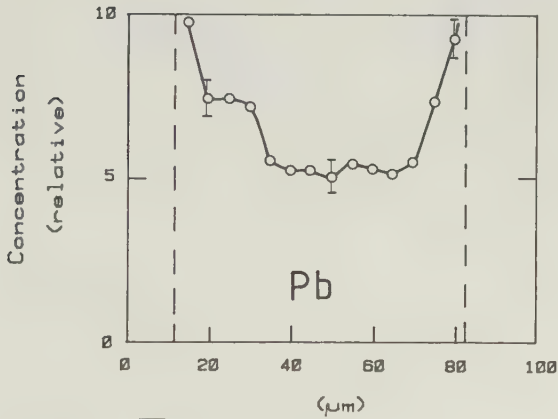


Figure 3(e) Results of the microbeam PIXE scan of hair-1 for lead. For other details see caption to fig.3(a).

Hair-2

The results are shown in figs 4(a)-(d). The measured yields of the chlorine K X-rays coincide perfectly with the calculated curve for the surface distribution. The X-value is 1.00. The calculated amount of chlorine is $(0.210 \pm 0.021) \mu\text{g}/\text{cm}$, and corresponds to a salt (NaCl) layer of thickness $(0.076 \pm 0.008) \mu\text{m}$ on the surface of the hair.

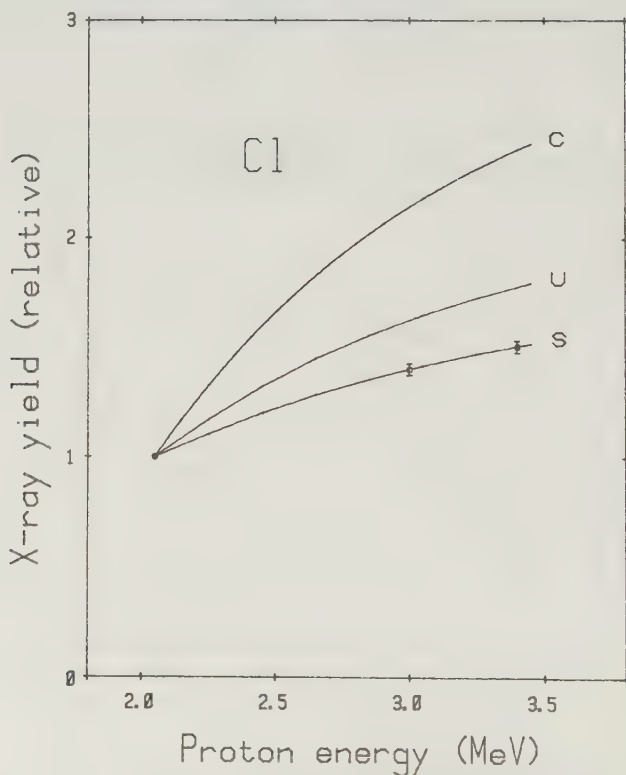


Figure 4(a) Results of the macrobeam PIXE measurements on hair-2 for chlorine. The hair diameter is $(66 \pm 2) \mu\text{m}$. For other details see caption to fig.2(a).

The measured yields of sulphur are very close to the u-curve. The X-value for the sulphur distribution in this hair is -0.19 . Hence, sulphur has a uniform bulk distribution, with a little lower concentration on the surface than at the centre. The calculated bulk concentration of sulphur is $(4.19 \pm 0.42)\%$ in this hair.

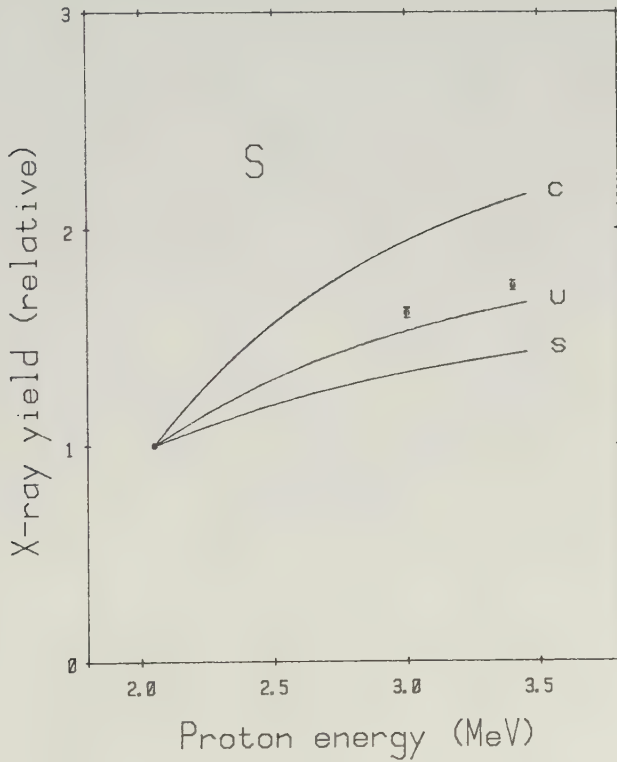


Figure 4(b) Results of the macrobeam PIXE measurements on hair-2 for sulphur. For other details see caption to fig.4(a).

The X-value for the calcium distribution in this hair is 0.15. It is basically a uniform bulk distribution, perhaps with a little higher concentration on the surface than at the centre of the hair. The calculated average bulk concentration of calcium is $(1.17 \pm 0.12)\%$.

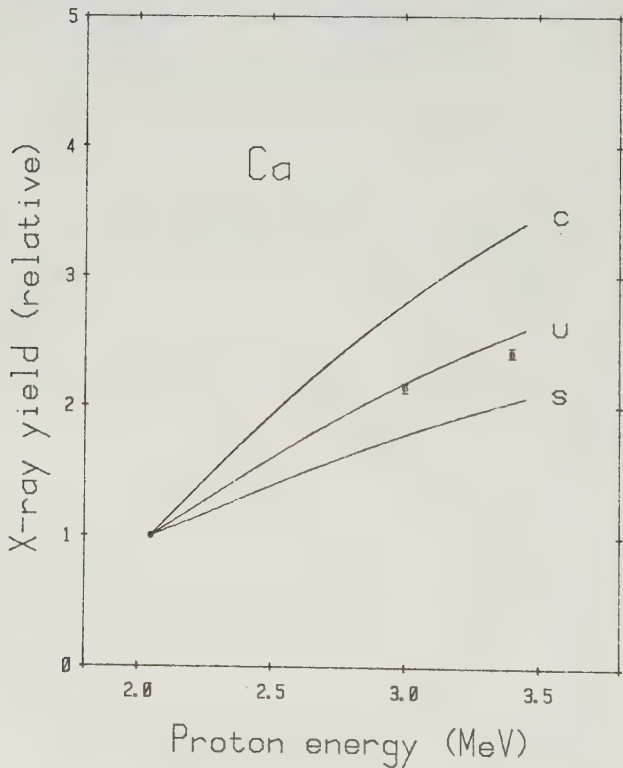


Figure 4(c) Results of the macrobeam PIXE measurements on hair-2 for calcium. For other details see caption to fig.4(a).

The X-value for the copper distribution in this hair is 0.18. Therefore, in this hair the distribution of copper is similar to the distribution of calcium. The calculated average bulk concentration of copper is (620 ± 78) ppm.

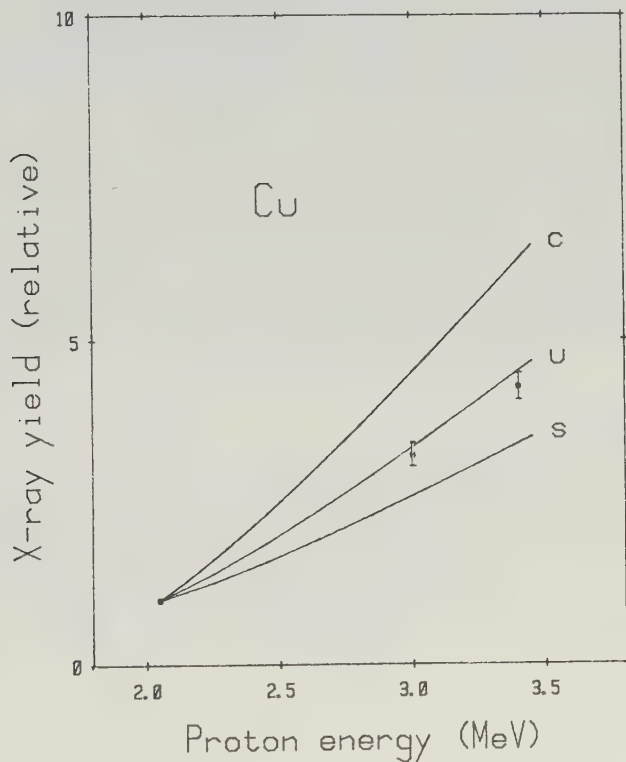


Figure 4(d) Results of the macrobeam PIXE measurements on hair-2 for copper. For other details see caption to fig.4(a).

5. Conclusions

A convenient method for qualitative determinations of radial elemental distributions in hairs is described. Results obtained from this method applied to a hair strand with a high lead content were compared with results from a radial scan of the same hair strand using a PIXE microprobe. The agreement is good indicating the usefulness of the method.

A second hair strand with a high concentration of chlorine was also analysed. The results are in accordance with a uniform bulk distribution of sulphur at a concentration of 4.2%, which further supports the feasibility of the method. The chlorine was shown to have a surface distribution - a fact supporting an exogeneous source.

Using the PIXE method at two (or more) different beam energies it is easy to differentiate between surface distributions, homogeneous bulk distributions and central distributions. For many applications this kind of qualitative information may be sufficient. To evaluate how detailed information the method can provide, further tests and calculations have to be performed.

Acknowledgements

We thank Mr. L.-E. Carlsson for the development of the proton microprobe in Lund, and for assistance during the experiment. We thank also Prof. K.R. Akselsson for valuable discussions throughout this work. This work was supported in part by the Ministry of Education, Beijing, China and by the Swedish Natural Science Research Council.

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Appendix: The calculation of F_S and F_C .

F_S is defined by the equation

$$F_S = \frac{1}{S} \int \frac{\sigma_X(E)}{\sigma_X(E_0)} \cdot T \cdot dS \quad (I)$$

where σ_X is the X-ray production cross section (which is a function of the proton energy E), E_0 is the incident proton energy, T is the X-ray transmission, and S is the surface area.

Fig.5 shows a cross sectional plane, defined by the trajectory of the incident protons and the diameter of the hair. It is apparent that

$$\begin{aligned} F_S &= \frac{1}{S} \left(\int_{S_f} \frac{\sigma_X(E)}{\sigma_X(E_0)} \cdot T \cdot dS + \int_{S_r} \frac{\sigma_X(E)}{\sigma_X(E_0)} \cdot T \cdot dS \right) = \\ &= 0.5 + \frac{1}{S} \int_{S_r} \frac{\sigma_X(E)}{\sigma_X(E_0)} \cdot T \cdot dS \end{aligned} \quad (II)$$

where S_f and S_r are the front and rear halves of the surface area S , respectively.

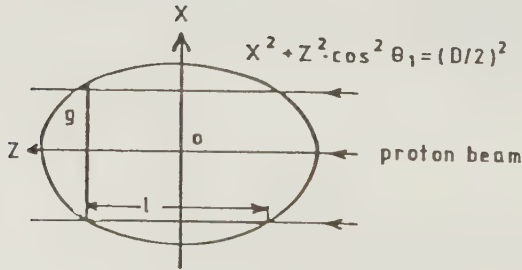


Figure 5 A cross sectional plane defined by the trajectory of the incident protons and the diameter of the hair in vertical direction.

Since $g^2 + (l \cdot \cos \theta_1)^2 = D^2$ so a parameter ϕ can be introduced such that

$$g = D \cdot \cos \phi \quad (\text{III})$$

and

$$l \cdot \cos \theta_1 = D \cdot \sin \phi \quad (\text{IV})$$

The differential element dS in eq.(II) can be thus expressed as follows

$$\begin{aligned} dS &= \frac{1}{2} ((d \cdot g)^2 + (d \cdot l)^2)^{\frac{1}{2}} = \\ &= \frac{D}{2 \cos \theta_1} (1 - \sin^2 \theta_1 \cdot \sin^2 \phi)^{\frac{1}{2}} d\phi \end{aligned} \quad (\text{V})$$

Accordingly,

$$S = \frac{D}{2 \cos \theta_1} \int_0^{2\pi} (1 - \sin^2 \theta_1 \cdot \sin^2 \phi)^{\frac{1}{2}} d\phi \quad (\text{VI})$$

Hence,

$$F_S = 0.5 \cdot \left(1 + \frac{\int_0^{\pi/2} \frac{\sigma_x(E)}{\sigma_x(E_0)} \cdot T \cdot (1 - \sin^2 \theta_1 \cdot \sin^2 \phi)^{\frac{1}{2}} d\phi}{\int_0^{\pi/2} (1 - \sin^2 \theta_1 \cdot \sin^2 \phi)^{\frac{1}{2}} d\phi} \right) \quad (\text{VII})$$

where σ_x and T are evaluated in the same way as in the calculation of F_u (ref.14).

The expression for F_c is straightforward

$$F_C = \left(\frac{\sigma_x(E)}{\sigma_x(E_0)} \cdot T \right)_{l=0.5D/\cos \theta_1} \quad (\text{VIII})$$

where l is the proton penetration depth (cm) in hair, and D is the hair diameter.

Fig.6 shows the results of the calculation of the correction factors F_s , F_u and F_c for a hair of diameter $70 \mu\text{m}$ in case where the incident proton energy is 2.55 MeV, and the beam-hair-detector geometry is as shown in fig.1, where $\theta_1 = \theta_2 = 22.5^\circ$.

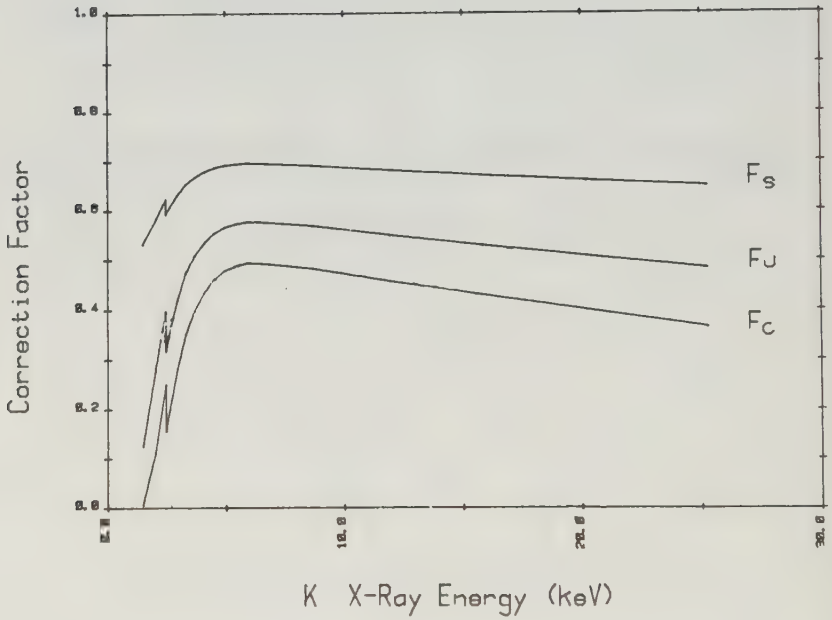


Figure 6 The calculated correction factors F_s , F_u and F_c for a hair of diameter $70 \mu\text{m}$. The incident proton energy E_0 is assumed to be 2.55 MeV. The beam-hair-detector geometry is as shown in fig.1, where $\theta_1 = \theta_2 = 22.5^\circ$.

PROTON BACK-SCATTERING - A TOOL FOR QUANTIFICATION OF THE RESULTS OF PIXE ANALYSIS OF SINGLE HAIR STRANDS

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As shown in a companion paper the geometrical diameter of a hair strand is an important parameter for quantification of its trace element content after PIXE analysis. By analysing the back-scattered protons simultaneously with PIXE analysis a reliable estimate of the hair diameter can be obtained. In this work the hypothesis that there exists a linearity between the geometrical diameter and the number of back-scattered protons in a certain energy interval is developed, discussed and experimentally verified.

1. Introduction

Proton back-scattering, PBS, in connection with the normalisation problem in the longitudinal scanning of a single hair strand with a normal millimetre proton beam, has been the topic of several recent papers (refs 1-4). Their main issue is the correlation between the number of back-scattered protons and the linear density (mass per unit length) of the hair strand. However, as shown in a recent paper (ref.5), the geometrical thickness of the hair strand is a better parameter for the normalisation of PIXE data than the linear density. Since variation of the thickness of a single hair strand during its growth is a rather common phenomenon, it is often necessary to determine the value of the thickness at each point included in the PIXE scan. In this paper a proper quantitative formulation of PBS

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applied to a single hair strand, under a beam-hair-detector geometry identical to the geometry proposed in ref.5, is described. In this formulation a linear measure of the thickness of the hair strand is obtained, which can be used for convenient and reliable quantification of PIXE data from each analysis point.

2. Theory

The beam-hair-detector geometry is schematically shown in figure 1(a). Figure 1(b) shows the path of the back-scattered protons. The path out, l_2 , is related to the path in, l_1 , by the formula

$$l_2 = \beta \cdot l_1 \quad (1)$$

where

$$\beta = \cos \theta_1 / \cos(\pi - \phi + \theta_1) \quad (2)$$

where θ_1 is the angle defined by the incident proton beam and the normal of the hair strand, and ϕ is the scattering angle in the laboratory system. The lengths l_1 and l_2 can be calculated using the formulae (ref.5)

$$l_1 = l_{m1} / \rho_0 = (2.35/\rho_0) \cdot (E_0^{1.70} - E^{1.70}) \quad (3)$$

and

$$l_2 = l_{m2} / \rho_0 = (2.35/\rho_0) \cdot ((K_A \cdot E)^{1.70} - E_1^{1.70}) \quad (4)$$

where ρ_0 is the density of the hair matrix, l_{m1} and l_{m2} are the lengths of the paths in the hair into and out of the scattering point (expressed in mg/cm^2), E_0 is the energy of the incident protons at the surface of the hair, E is the proton energy just before scattering, $(K_A \cdot E)$ is the proton energy just after scattering from a target atom of atomic weight A in the angle ϕ of the laboratory system, and E_1 is the energy of the proton on leaving the surface of the hair. For elastic collisions the kinematic factor K_A is given by

$$K_A = ((\cos \phi + (A^2 - \sin^2 \phi)^{\frac{1}{2}}) / (A+1))^2 \quad (5)$$

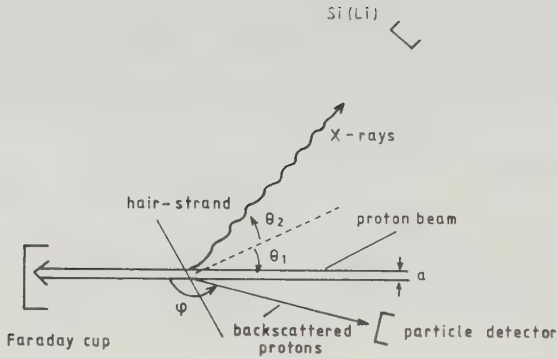


Figure 1(a) The beam-hair-detector geometry (horizontal plane).
The dashed line is the normal to the hair segment.

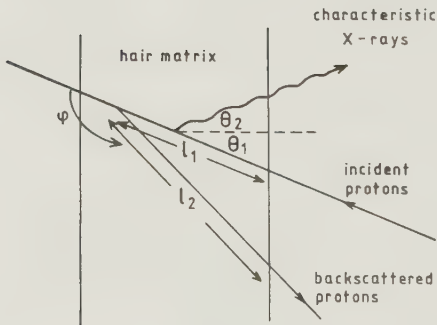


Figure 1(b) Path of the back-scattered protons.

Combining eqs (1) - (4) results in

$$E = E_0 \cdot ((E_1 / (K_A \cdot E_0))^{1.70} + (\beta / K_A^{1.70})) / (1 + \beta / K_A^{1.70})^{1/1.70} \quad (6)$$

and

$$l_{m1} = 2.35 / (K_A^{1.70} + \beta) \cdot ((K_A \cdot E_0)^{1.70} - E_1^{1.70}) \quad (7)$$

Hence

$$\Delta l_{m1} = -4.0 / (\beta + K_A^{1.70}) \cdot E_1^{0.70} \cdot \Delta E_1 \quad (8)$$

The number of back-scattered protons with an energy between $E_1 - \Delta E_1/2$ and $E_1 + \Delta E_1/2$ is equal to

$$H(E_1) \cdot \Delta E_1 = \sum_A \frac{N_p}{a \cdot b} \cdot \frac{C_A \cdot \Delta m}{A} \cdot N_0 \cdot \sigma_A(E, \phi) \cdot \Omega \quad (9)$$

where N_p is the total number of protons collected in the Faraday cup, a and b are the dimensions of the proton beam in the horizontal and vertical directions respectively as defined by the collimator, C_A is the mass concentration of the element of atomic weight A , N_0 is Avogadro's number, $\sigma_A(E, \phi)$ is the differential scattering cross section for protons of energy E from an element of mass A with the scattering angle ϕ , and Ω is the solid angle. The mass element Δm is defined, as shown in fig.1(c), as follows

$$\Delta m = a \cdot g \cdot \Delta l_{m1} = a \cdot (D^2 - l_{m1}^2 \cdot \cos^2 \theta_1 / \rho_0^2)^{\frac{1}{2}} \cdot \Delta l_{m1} \quad (10)$$

where D is the diameter of the hair. Replacing l_{m1} and Δl_{m1} in eq.(10) with eqs (7) and (8), and Δm in eq.(9) with eq.(10) results in

$$H(E_1) = \sum_A H_A(E_1) \quad (11)$$

$$H_A(E_1) = H_A(K_A \cdot E_0) \cdot \left(\frac{E_1}{K_A \cdot E_0} \right)^{0.70} \cdot \frac{\sigma_A(E, \phi)}{\sigma_A(E_0, \phi)} \cdot \eta_A \quad (12)$$

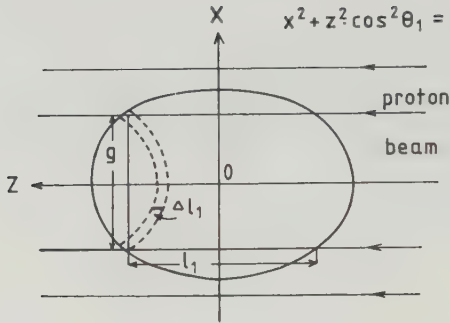


Figure 1(c) The mass element $\Delta m = \rho_0 \cdot \Delta V = \rho_0 \cdot a \cdot g \cdot \Delta l_1 = a \cdot g \cdot \Delta l_{m1}$
 where $g = (D^2 - l_1^2 \cdot \cos^2 \theta_1)^{\frac{1}{2}}$.

$$H_A(K_A \cdot E_0) = \frac{N_p}{b} \cdot \frac{C_A}{A} \cdot N_0 \cdot D \cdot \frac{4.0(K_A \cdot E_0)^{0.70}}{\beta + K_A^{1.70}} \cdot \sigma_A(E_0, \phi) \cdot \Omega \quad (13)$$

$$\eta_A = (1 - \gamma_A \cdot (1 - (\frac{E_1}{K_A \cdot E_0})^{1.70})^2)^{\frac{1}{2}} \quad (14)$$

$$\gamma_A = (2.35 \cdot \cos \theta_1 \cdot (K_A \cdot E_0)^{1.70} / (D \cdot \rho_0 \cdot (\beta + K_A^{1.70})))^2 \quad (15)$$

where E can be evaluated using eq.(6) and K_A using eq.(5). Eqs (11) - (15) describe the PBS process for a single hair strand, and provide the necessary knowledge for its practical application.

Of immediate interest is the fact that $H(E_1)$ is linearly proportional to the geometrical thickness D of the hair strand when the factor $\eta_A \approx 1$. This property may be used to determine the thickness of the single hair strand in connection with PIXE scanning analysis. For $\theta_1 = 22.5^\circ$, $\phi = 160^\circ$, $E_0 = 2.55$ MeV, $D = 40 \mu m$ and $E_1 \geq 1.5$ MeV it was found that $0.96 \leq \eta_A \leq 1$.

3. Experiment

Hair strands from 8 individuals (3 females and 5 males from China, Finland and Sweden) were collected. The hair strands were ultrasonically cleaned in deionized water for about 10 minutes and then dried at normal room temperature. 53 hair segments, each about 2 cm long, were prepared from the hair strands. Each hair segment was glued in the same position on identical aluminium frames. No backing material was used. The thicknesses of the hair segments were measured with a microscope both before and after the experiment. Since a hair segment only 2 cm long still does not have a uniform thickness, it is important to measure the diameter of the hair at the exact position where the proton beam has hit or will hit. For positioning of the frames in the microscope, a "position reference" was used. This was a hair segment mounted as all the other segments, but burned by an intense beam, so that the beam position on the hair could be identified easily.

The beam-hair-detector geometry used in the experiment is as shown in fig. 1(a), where $\theta_1 = \theta_2 = 22.5^\circ$ and $\phi = 160^\circ$. A detailed description of the irradiation chamber can be found in the literature (ref.6). The beam is first diffused by a gold foil, and its central part is then picked out through the $2.0 \times 4.0 \text{ mm}^2$ collimator. The proton energy after the diffusing foil is $E_0 = 2.55 \text{ MeV}$, and the beam current after the collimator is kept below 10 nA to avoid heating damage to the hair segments during irradiation. The thickness of the hair segment was found not to change due to the proton bombardment (the uncertainty in the microscopic determination was $\pm 2 \text{ }\mu\text{m}$). PBS spectra from the 53 hair segments were recorded. The integrated proton charge was $2.0 \text{ }\mu\text{C}$ for each spectrum.

4. Results

Fig.2 shows a typical PBS spectrum from this investigation. The number of counts between channel 243 ($E_1 = 1.53 \text{ MeV}$) and channel 272 ($E_1 = 1.78 \text{ MeV}$) in the 53 spectra is plotted in fig.3 against the hair thickness measured with the microscope. The choice of channel 243 and channel 272 is made by considering the following factors: a) The lower limit of the energy interval should be as high as possible to satisfy

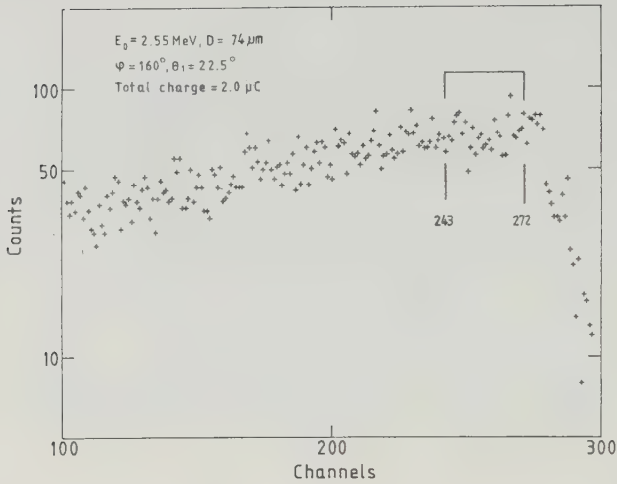


Figure 2 A typical PBS spectrum from a single hair strand. In this work the number of counts between channels 243 and 272 is used as a measure of the hair diameter.

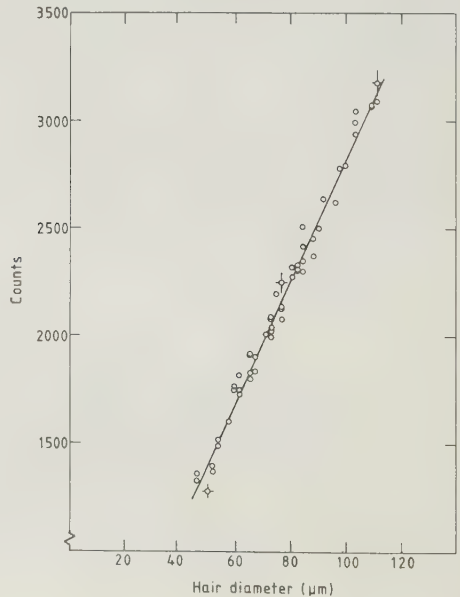


Figure 3

The number of back-scattered protons, as defined in fig.2, as a function of the hair diameter.

the linearity condition $\eta_A \approx 1$; b) The higher limit of the energy interval should be kept some distance from the "jumps" of the PBS spectra to avoid irrelevant complexities such as the energy resolution of the detection system; c) The energy interval should be large enough to include a sufficient number of counts for good statistics. The data in fig.3 are fitted by a linear least-squares fit. The discrepancies between the fitted line and the measured points are less than 5 μm . The agreement is thus good demonstrating the linear relationship between the number of counts and the geometrical thickness of a single hair strand.

5. Discussion

Whitehead (ref.1) and Campbell et al. (refs 2-4) tried to use PBS to determine the mass of the bombarded part of a hair strand, but were unfortunately not very successful. The reason is that hair from a human scalp is usually not thin enough, in relation to the energy of the proton beam normally used in PIXE work, so that all of the protons back-scattered from different parts of the hair have a sufficient energy to travel out from the hair matrix. A 2.55 MeV proton, for example, can well penetrate a hair of 70 μm in diameter in an arrangement such as the one shown in fig.1(a) with $\theta_1 = 0^\circ$, but it can not travel out from the hair matrix if it hits a nucleus of carbon, nitrogen or oxygen at a penetration depth greater than 35 μm , and then scatters back at an angle $\phi = 160^\circ$. Therefore, PBS is only sensitive to a certain part of the hair mass being bombarded. The correlation between this sensitive part and the remaining insensitive part varies with the hair thickness, and becomes rather uncertain if taken into consideration complexities such as the cross section of some hair not being round, and the mass density of different hairs not exactly being the same etc.

The method presented in this paper is not only limited to hair samples. Indeed, it has a very general nature, and is especially suitable for biological samples. In cases where the specimen can not be considered as thin in connection with PBS as discussed above, an alternative to the determination of the total mass being bombarded is to determine the geometrical area of the specimen being bombarded. The number of back-scattered protons in a certain energy interval is

linearly proportional to the geometrical area of the bombarded part of a layer of a certain thickness (mg/cm^2) of the specimen at a certain depth (mg/cm^2) if the major elements of the specimen do not differ very much from each other in their atomic weight (except hydrogen, which is not sensitive to PBS).

The energy interval 1.53–1.78 MeV, chosen in fig.2, corresponds to a layer in hair roughly between the geometrical penetration depths 2.8 μm and 8.8 μm (Notice that the proton beam penetrates the hair at an angle $\theta_1 = 22.5^\circ$ in our experiment). As the dimension along the length of the hair has been fixed by the beam size, a , in the horizontal direction, the number of counts within the chosen energy interval is therefore linearly proportional to the geometrical size of the layer in the vertical direction. By simple geometric calculation, the average size of the chosen layer in the vertical direction turns out to be 39.6 μm , 79.8 μm , and 119.9 μm if the diameter of the hair is assumed to be 40 μm , 80 μm , and 120 μm respectively. This explains in a straightforward manner the foundation of the method described.

It may be worthwhile to mention one more point: back-scattered protons from the (p , p') resonance of ^{12}C at a proton energy of 1.74 MeV will be trapped within the hair matrix if the incident proton energy is higher than a certain value, e.g. 2.2 MeV in our experiment. This appears to be a good way to get rid of the resonance peak when acquiring a PBS spectrum from a thick biological sample.

Acknowledgements

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A PIXE SYSTEM FOR ROUTINE LONGITUDINAL SCANNING OF SINGLE HAIR STRANDS

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This article describes a PIXE system designed and constructed for routine longitudinal scanning of single hair strands. In constructing a PIXE system for trace elemental scans of single hair strands on a routine basis, a fairly intense beam has to be used but the heating damage must be kept to a minimum. The experimental conditions (charge integration, beam homogeneity etc.) have to be carefully controlled in order to give accurate PIXE results. The geometrical thickness of the hair at each point of the scan has to be determined and a qualitative knowledge of the elemental distribution over the cross section of the hair has to be provided for a proper interpretation of the PIXE results. In the present PIXE system the geometrical thickness of a hair strand at each point along the scan is determined by counting the number of back-scattered protons simultaneously with the PIXE analysis and a qualitative knowledge of the elemental distribution over the cross section of the hair is obtained through bombarding the hair at particular points with different proton energies.

1. Introduction

As the trace element levels in human hair may reflect the course of the corresponding blood plasma concentrations, hair analysis for trace elements is of increasing interest both in nutrition research and in toxicology (refs 1-8). One of the advantages of the PIXE technique is its low mass detection limits for small samples (ref.9). A piece of

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hair 1 mm in length and 60 μm in diameter weighs about 3.7 μg and a trace element at the 10 ppm level in mass concentration amounts to only 0.037 ng. This small amount would be a problem for many other techniques but for PIXE it is well above the mass detection limits for most of the metal trace elements. Two early papers demonstrated the potential of the PIXE technique for trace element profiling along an individual's hair (refs 10-11). Although it is relatively easy to expose a hair to a proton beam from an electrostatic accelerator and record the X-ray spectrum emitted using a Si(Li) detector, it is much harder to quantify the results (ref.12). Montenegro et al. (ref.13) proposed a correction factor to account for the effects of the energy loss of the incident particle with penetration depth, and X-ray self-absorption by introducing some simplifying approximations. The approximations, as pointed out in a recent paper (ref.14), are rather crude for lighter elements. Much effort was put into finding a procedure for accurate determination of the mass of the hair from which the X-rays originate (refs 12, 15-16). Campbell et al. (ref.16) reported a method in which the PIXE scanning of an individual hair with about 1 mm spatial resolution provided a position dependence of trace element concentrations in relative terms and the subsequent conversion of the hair to a thin specimen for PIXE analysis provided absolute trace element concentrations for the entire hair. However, this method is only suitable for hair with a fairly constant thickness (ref.14). Neither the characteristic X-ray intensity at each point of the scan nor that from normalizing this intensity to the linear density (g/cm) of the hair can be taken as a relative measure for the concentration of the trace element if the linear density varies considerably along the whole length of the hair.

This article describes a PIXE system which uses a rectangular proton beam of millimetre size for routine longitudinal scanning of single hair strands. To make clear the discussions which follow, the following simple expression may be helpful:

$$\rho_1 = \frac{N_x}{(Q/b) \cdot P \cdot F}$$

where ρ_1 is the linear mass density of the trace element along the hair (g/cm), N_x is the number of counts in the characteristic X-ray peak, Q is the total charge of the protons collected in the Faraday cup (μC), b is the size (cm) of the proton beam in the vertical

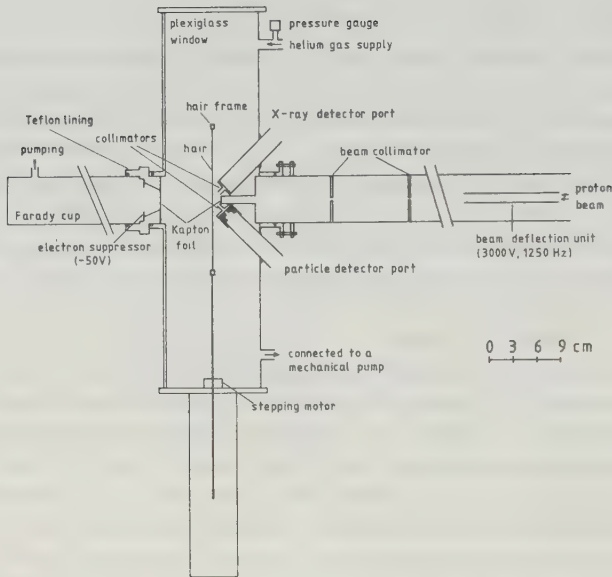


Figure 1 Irradiation chamber for routine PIXE scanning of single hair strands (horizontal plane).

direction (the hair strand is horizontally positioned), P is the sensitivity factor for thin foils ($\text{counts} \cdot \text{cm}^2 / (\mu\text{C} \cdot \text{g})$) and F is the correction factor for proton energy loss and X-ray absorption in the bulk of the hair. Therefore, the accuracy in the elemental concentrations obtained depend on the accuracy in counting the X-ray pulses, in charge integration, in obtaining a homogeneous beam intensity profile, in determining the beam width b , in the system mass calibration, and in evaluating the magnitude of the correction factor F . The method of calculating the correction factor F is discussed elsewhere (ref.14); we argue there that the geometrical thickness of a hair strand is a more proper parameter for normalization of the PIXE data than the linear density (g/cm) and a qualitative knowledge of the elemental distribution over the cross section of the hair would significantly reduce the uncertainty in the calculation.

2. Experimental

The irradiation chamber of the system is shown in fig.1. To reduce the heating damage in the hair strand during scanning the chamber is filled with 600 mb helium. The hair strand is fixed on a Teflon frame supported by an aluminium holder, which is driven by a computer-programmed stepping motor. The hair strand is kept moving longitudinally back and forth to minimize the heating damage due to a prolonged irradiation of the same point of the hair strand. Accordingly, up to 16 memory groups are assigned for acquiring PIXE spectra during the scan. A hair strand can only withstand a beam intensity of about 1 nA/mm^2 in vacuum under prolonged irradiation of 2-3 MeV protons. Currents above 2 nA/mm^2 would result in damage which is apparent to the eye. With a helium atmosphere the beam intensity can be raised to $2-3 \text{ nA/mm}^2$, but above 5 nA/mm^2 will most likely result in obvious damage. The beam intensity can be raised to above 10 nA/mm^2 by continuously moving the hair strand back and forth in a helium atmosphere. The chamber is isolated from the beam line vacuum by a Kapton foil of thickness $7.5 \mu\text{m}$ (the entrance of the proton beam into the helium chamber) and from the Faraday cup by a Kapton foil of $25 \mu\text{m}$ (the exit of the proton beam from the helium chamber). The protons, when striking the $25 \mu\text{m}$ Kapton foil, will produce secondary electrons which may enter the Faraday cup and interfere with the charge measurement. To suppress these secondary electrons, a metal ring (at a potential of -50 Volts) is placed between the exit foil and the Faraday cup. It is suspected that whether the helium atmosphere in chamber influences the charge measurement. In fig.2 the number of silver K X-ray counts per unit measured charge from a thin foil is plotted versus the helium pressure. It is shown that the helium atmosphere in this chamber from zero to one atmospheric pressure does not interfere the charge measurement significantly, and the proton energy loss over the path from the $7.5 \mu\text{m}$ entrance foil to the hair strand can be neglected due to the very close geometry. The chamber windows for the X-ray detector and for the proton back-scattering measurement are made of $12 \mu\text{m}$ Kapton foils. Between the two windows and the hair strand are the two collimators which allow only X-rays and back-scattered protons originating from the hair to enter the sensitive volumes of the two detectors. A pair of tantalum collimators separated by 10 cm in the beam line allows the selection of a proper

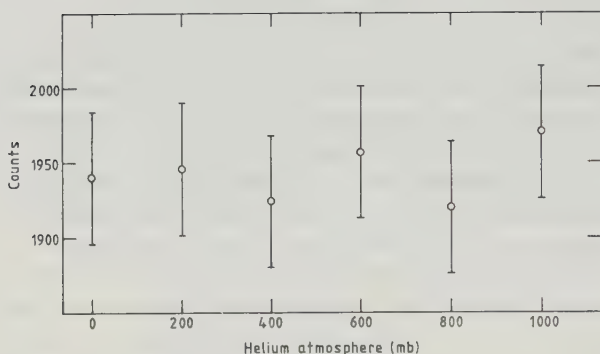


Fig.2 Number of silver K X-ray counts per unit measured charge from a thin foil plotted versus the helium pressure. The indicated errors are statistical (one S.D.).

beam size. The width of the collimators in the horizontal direction determines the spatial resolution of the scan while a sufficient width of the collimators in the vertical direction allows a certain degree of uncertainty in positioning the hair. In order to achieve a homogeneous beam intensity profile along the vertical direction while maintaining the necessary beam intensity, the proton beam is swept electrostatically by a triangular voltage applied to a pair of parallel plates in the beam tube. For the system mass calibration, thin homogeneous standards from MicroMatter Co were used. A detailed description of the method of system mass calibration can be found in the literature (ref.17).

3. Results and discussion

Fig.3 shows a longitudinal PIXE scan of a hair strand (6 cm in length) for Cu, Pb and Hg levels. The integrated charge for each point is $4.95 \mu\text{C}$. The whole scan takes about one hour. The geometrical thickness of the hair strand at each point along the scan is determined by simultaneously counting the back-scattered protons. It has been proved in a previous paper (ref.18) that the number of

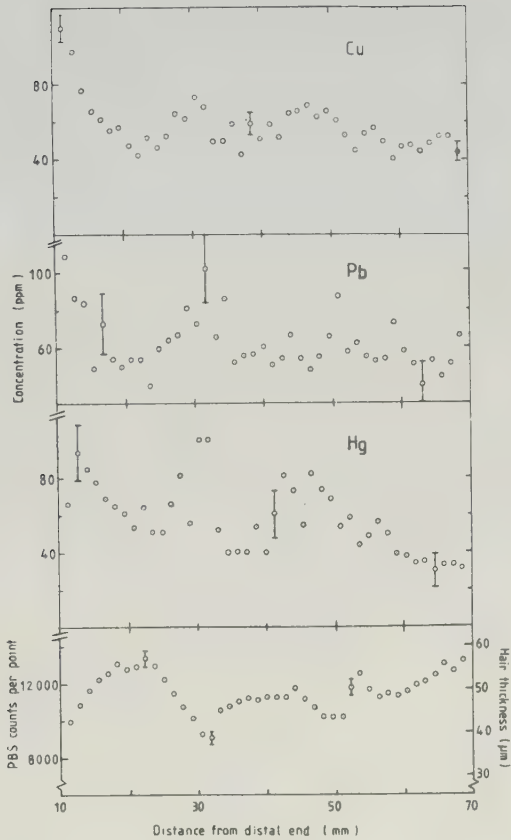


Figure 3 A longitudinal PIXE scan of a hair strand for Cu, Pb and Hg concentrations. PBS counts per point refers to the number of back-scattered protons in the chosen energy interval.

back-scattered protons in a chosen interval in the high energy region of the PBS spectrum is linearly proportional to the geometrical thickness of the hair strand. Therefore, the number of back-scattered protons in the energy interval can be readily converted into the geometrical thickness of the hair strand at the point of the scan once the system is calibrated with hair segments of known thicknesses (as determined with e.g. a microscope). The quantification of the PIXE data in mass concentration (g/g) is made by assuming that the trace elements are homogeneously distributed over the cross section of the hair (refs 14,19).

Fig.4(a) shows a scan of a hair strand which contains an extremely high lead concentration. The lead concentration increases from the root end to its tip. It is therefore suspected that this is due to external contamination. To further support this assumption, a piece of the hair was bombarded with protons of different energies. The relative yield of Pb L_{α} X-rays is expected to increase with proton energy. Moreover, the relative yield curves should be different for different elemental distributions over the cross section of the hair. Three curves are calculated (ref.19), as shown in Fig.4(b), and

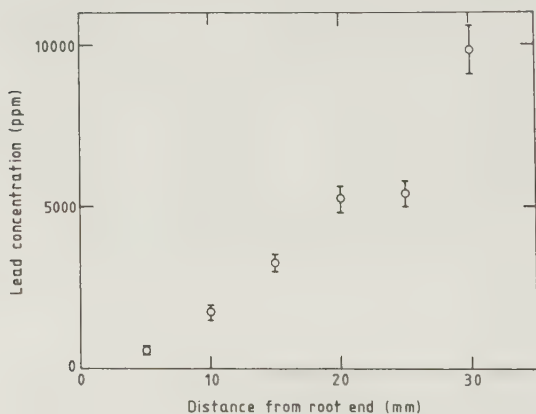


Figure 4(a) A longitudinal PIXE scan of a hair strand for Pb concentration.

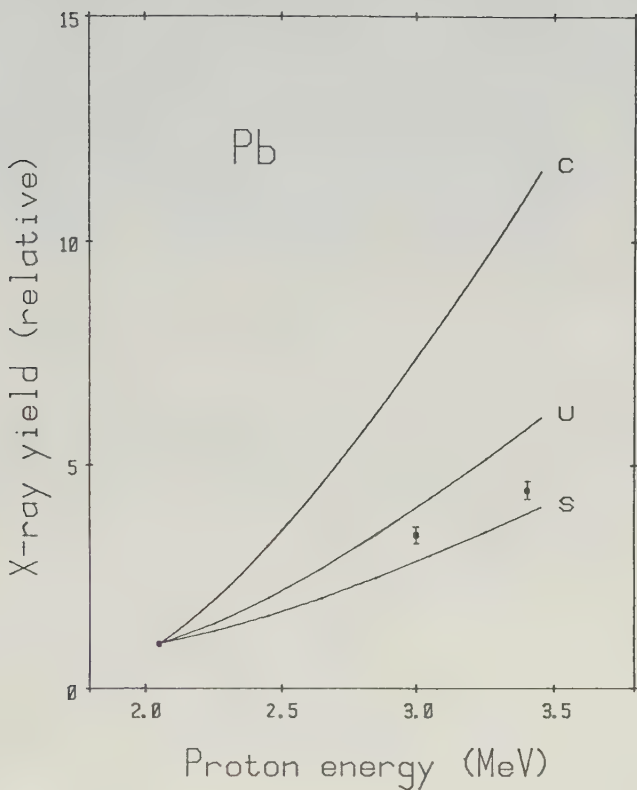


Figure 4(b) The relative yields of Pb L_{α} X-rays (normalized to the yield at 2.05 MeV proton energy). The three curves denoted by the letters s, u and c are calculated ones (ref.19) corresponding a surface elemental distribution, a uniform bulk distribution and a central distribution respectively; the points are the experimental data. The indicated errors are statistical (one S.D.).

correspond to three different cases: s denotes that the lead is completely distributed on the surface of the hair, u denotes a uniform distribution in the bulk of the hair and c denotes that the lead content is completely concentrated at the centre of the hair. The experimental data turn out to be somewhere between the surface distribution and the uniform distribution. This suggests that the lead content of this hair, if it is due to external contamination, has already entered into the bulk of the hair by diffusion. A detailed discussion of the use of millimetre proton beams to determine the elemental distribution across the diameter of a hair is given elsewhere (ref.19).

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